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Reactive wetting behaviors of Sn/Cu systems: A molecular dynamics study

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Influences of temperature and Sn-Cu droplet’s composition on reactive wettings of Cu(100), Cu(110), and Cu(111) surfaces were analyzed, by using molecular dynamics (MD) calculations. As a result, the spreading on Cu(110)/(Cu(100)) has the fastest (slowest) wetting kinetics. A higher temperature or a diluter Cu content in the Sn-Cu alloy droplet results in a higher wettability. Moreover, this work has addressed a theory for positioning the interface separating the liquidus and solidus alloys in the spreading film to confirm the hypothesis that the reactive wetting will come to the end when the interface saturates with the temperature-dependent solidus weight fraction of Cu.

Keywords: Wetting; Surface alloying; Molecular dynamics; Droplet

Citation: J. Y. Hsieh, J. L. Chen, C. Chen, H. C. Lin, S. S. Yang and C. C. Hwang, “Reactive wetting behaviors of Sn/Cu systems: A molecular dynamics study”, Nano-Micro Lett. 2, 60-67 (2010). doi: 10.5101/nml.v2i2.p60-67

In recent years, lead free solders have been extensively proposed in utility of connecting devices to printed-circuit boards in microelectronic manufacturing because of legal, environmental and technological considerations [1]. In the soldering process, a metallurgical bond is formed between a molten solder and a metal surface. Therefore, the molten solder is required to properly spread, or wet, on the metal substrate for the formation of a proper metallic bond. The tendency for a metal to spread on a solid surface has been defined as the wettability [2]. In the case of inert liquid/solid combinations, the wettability can be evaluated by calculating the contact angle between the solder and the substrate via Young’s equation, which gives the balance of the solid surface/gas, solid/liquid, and gas/liquid interfacial tensions at equilibrium. Nevertheless, Young’s equation is less useful for the realistic soldering process, where the mechanical strength of a material joint depends significantly on the degree of reaction between the spreading solder and the solid substrate. Even so, a lower contact angle between the solder and the substrate in general corresponds to a lower surface interfacial energy and indicates a higher wettability. Particularly, surface alloying, which is resulted from the reaction between the solid surface and the liquid spreading on it, has been observed to improve wettability [3]. Therefore, reactive wettings are of particular interest in studies relevant to lead free soldering.

Acoff and coworkers [4,5], using sessile-droplet method, have reported the contact angle measurements of four lead free Sn-based alloys, namely Sn-3.5Ag, Sn-3.5Ag-4.8Bi, Sn-3.8Ag-0.7Cu, and Sn-0.7Cu (wt.%), on copper substrates. They found the Sn-3.5Ag-4.8Bi alloy exhibited the lowest contact angles indicating improved wettability with addition of bismuth and the contact angle decreased with increasing temperature, depending on the type of flux used in the sessile-droplet method. Amore et al. [6] have experimentally studied the surface tension and wetting behavior of molten Cu-Sn alloys on Ni substrate. They found their results of the surface tension of the Cu-Sn system are in good agreement with

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the works of Drath et al. [7] and Lee et al. [8] and concluded that the contact angle decreases with the increase of Sn-content for the Sn-rich Cu-Sn alloys. Other experimental studies on the wetting behavior of Sn-based lead free solders on metal substrate can also be found in refs [9-17].

Besides experimental methods, theoretical continuum models have also been proposed in studying the reactive wetting of solid surfaces [18-20]. However, continuum models inevitably make significant approximations because of lacking atomistic analyses of the wetting detail. Recently, molecular dynamics (MD) calculations have been implemented as atomistic simulations in researches of the reactive wetting since they are able to provide more robust constitution relations and more detailed surface transport mechanisms. Webb III and coworkers [21,22] studied the reactive wetting behaviors of liquid Pb and Ag on copper substrates, respectively. They demonstrated that in the liquid Pb wetting Cu(111) and Cu(100), a precursor film of atomic thickness spreads significantly faster on Cu(111) than on Cu(100) [21]. They also demonstrated that as liquid Ag spreads on Cu surface, wetting kinetics is enhanced by dissolution reactions [22].

In particular, knowledge of the reactive wetting of Sn/Cu systems is important for a lead free soldering process since Sn-Cu binary alloys can represent a basic subsystem of some Sn-based multi-element alloys proposed as alternative solder materials, such as Sn-Ag-Cu, Sn-Bi-Cu, and Sn-Ag-Cu-Sb, etc.. Relevant MD studies of the wetting of Cu substrate by pure Sn or Sn-Cu alloys, however, are rare. This work therefore attempts to perform MD calculations of the spreading of liquid Sn-Cu droplets, including a pure Sn droplet, on Cu crystals to study in detail the reactive wetting behaviors occurring within the liquid/solid system. This study is of two-fold interest. It is hoped to provide the physical insights of the wetting system and the necessary information required in a lead free soldering. The influences of the crystalline direction of the substrate surface, temperature, and the alloy droplet’s composition on wetting kinetics will be examined, respectively. The wettings by pure Sn droplet will first be investigated. Webb III et al. [21,22] have hypothesized that the reactive wetting is dominantly driven by the dissolution of the substrate atom into the liquid until the liquid saturates in the substrate atom. This work will rephrase this hypothesis by assuming that the dominant force will stop driving the reactive wetting as long as an interface separating the liquidus and solidus alloys in the spreading film saturates with the temperature-dependent solidus weight fraction of the substrate atom and stops moving into the liquid. This hypothesis will be confirmed through establishing a theory for positioning the liquid/solid interface and determining its saturation with the solidus weight fraction of the substrate atom. The correctness of the hypothesis and the usability of the theory will be re-verified by the results of the remaining wettings, by the liquid Sn-Cu alloys.

This study simulated the reactive wetting of pure Sn and Sn-Cu alloy droplets on Cu(100), Cu(110), and Cu(111) surfaces, respectively. Positions and velocities of both the droplet and the substrate atoms were calculated as functions of time using MD methodology. The Cu-Cu, Cu-Sn, and Sn-Sn interactions are described by modified embedded atom method (MEAM) potentials [23]. All MEAM parameters used in the present calculations are from the report of Aguilar et al. [24]. In each of the present simulations, the spreading was considered as an isothermal process that both the droplet and the substrate were controlled at a common temperature that is higher than the solidifying point of the droplet. Figure 1 shows the configuration of the droplet wetting system considered in this work. Four droplets of pure Sn and Sn-Cu alloys, namely, Sn-10Cu, Sn-20Cu, and Sn-30Cu (wt%), respectively, were considered. Each of the droplets, with a diameter of about 5nm, comprised a fixed number of 3000 atoms. The solidifying temperatures, or, the liquidus temperature, of these droplets, evaluated in the present trial simulations, are about \(T_{L_{Sn}}=450\text{K}, T_{L_{Sn10Cu}}=600\text{K}, T_{L_{Sn20Cu}}=650\text{K}, \) and \(T_{L_{Sn30Cu}}=850\text{K},\) respectively.

The MEAM liquidus and solidus temperatures of the nanometer scale Sn-Cu binary considered here as functions of the weight fraction of Cu, \(W_{Cu}^\text{L}\), are presented in Fig. 2. The droplet atoms were simulated as in free motion. Three FCC copper crystals were constructed as the substrates with the [100], [110], or [111] direction oriented along the z axis, respectively. The copper substrate was arranged in a finite slab with a lateral area of 106.50\(\text{Å} \times 106.50\text{Å}\) and thickness of 9.03\(\text{Å}\). The center of the droplet was positioned on z axis and the bottom of the droplet was positioned about 3\(\text{Å}\) above the Cu surface when the system has been in equilibration.

FIG 1. Configuration of the wetting system. Droplets of pure Sn and Sn-10Cu, Sn-20Cu, and Sn-30Cu (wt% \()\) were considered, respectively. Each droplet comprises 3000 atoms of Sn (red) and Cu (blue). Bottom of the substrate comprises two layers of rigid Cu atom. The origin of the coordinates is on the substrate surface. The center of the droplet was positioned on z axis and the bottom of the droplet was positioned about 3\(\text{Å}\) above the Cu surface when the system has been in equilibration.

DOI: 10.5101/nml.v2i2.p60-67
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The initial velocities. The initial positions of the (poration of Sn into the Cu lattice to fluid atom into the solid substrate, is the work, the alloy droplets with W

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dynamics was implemented to study the physical mixture of can also be seen in ref. [25], in which MEAM molecular

droplet is rational because the droplet is in liquid phase, as a function of the weight fraction of Cu.

thickness of 15.32 Å for the Cu(110) substrate, and with a lateral area of 131.83 Å × 131.83 Å and thickness of 16.63 Å for the Cu(111) substrate. The Cu(100), Cu(111), and Cu(110) substrates comprised 10800, 36608, and 28080 FCC copper atoms, respectively. The bottom of the substrate was two layers of rigid atoms and the remaining part of the substrate consists of free motion atoms. In the present MD simulations, periodic boundary conditions were applied in the directions in the plane of the free surfaces (x and y).

A constant time increment Δt=2 fs for integrating the equations of motion for all non-rigid atoms was employed in the present computations. Each MD simulation performed herein comprised the stage of the equilibration of the droplet/substrate system and the stage of spreading. The equilibration stage consumed a computation time of 20 ps, which is sufficiently long for the relaxation of both the droplet and the substrate. After this stage, the bottom of the droplet was positioned about 3 Å above the substrate surface such that the effect of the long-range attractive force between the drop and substrate can be avoided. The initial positions of the pure Sn droplet atoms were randomized and the substrate atoms were arranged in accordance with their crystalline structures, respectively. The arrangement of randomized positions of the Sn droplet is rational because the droplet is in liquid phase, as can also be seen in ref. [25], in which MEAM molecular dynamics was implemented to study the physical mixture of nano-Sn and nano-Ag particles. In this work, the influence of droplet composition was studied using binary Sn-Cu liquids. To do so, Cu atoms were randomly substituted for Sn atoms in the liquid to achieve the desired weight fraction of Cu, W_{Sn}^{Cu}. In this work, the alloy droplets with W_{Sn}^{Cu}=0.1, 0.2, and 0.3 were used in the wetting simulations, respectively. For all the cases studied here, the initial velocities of all atoms in the spreading

system were randomized according to the specific temperature using numbers uniformly distributed in an interval. The spreading stage then started when both the droplet and substrate have been relaxed to their equilibrium atomic configurations. The spreading stage lasted for 300 ps, which is long enough for the spreading process to become steady. In all the present MD simulations, the temperatures of the whole spreading system were held at a desired value using the rescaling method [26,27]. The leap-frog algorithm was implemented to derive new position and velocity vectors of the droplet and the substrate atoms from the corresponding data obtained in the previous step. The motion of each atom in the system was governed by Newton’s law of motion in which the resulting force acting on the atom was deduced from energy potential relevant to the interactions with the neighboring atoms within a cut-off radius.

In the studies of dissipative wettings of Cu substrates by liquid Pb and Ag, Webb III et al. [21,22] pointed out that dissolution of the substrate atom into the liquid drop, over the incorporation of the liquid atom into the solid substrate, is the dominant driving force of the reactive spreading until the liquid saturates in the substrate material. Like the Pb/Cu and Ag/Cu systems, for the present cases, a pure Sn or a Sn-Cu binary droplet placed on pure Cu will dissolve Cu into the droplet as it spreads. Accompanied with the dissolution of Cu, Sn will also be incorporated into the Cu lattice. However, attentions will be paid only on regimes where dissolution of solid into the liquid is dominant, because incorporation of Sn into the Cu lattice to form an equilibrium solid solution involves solid state diffusion that will consume a time far beyond the capability of atomistic simulations. In the present cases, since Sn droplet spreads on Cu substrate more quickly than Ag droplet does, the saturation of the liquid Sn droplet in Cu will be completed in a rather short time and therefore can be observed more sufficiently. In fact, all wettings simulated in this work have already come to the end before the simulation time of 300 ps. Figure 3 shows the cross-section snapshots from simulations when the wettings by the pure Sn droplet at 1000K have taken place for 300 ps on the three Cu substrates, respectively. During the spreading progress, surface alloying reaction on the substrate surfaces can be observed through the occurrence of the dissolution of Cu atoms into the liquid Sn droplet and the incorporation of Sn atoms into the Cu crystal. To quantify the wetting kinetics of the Sn droplet on Cu substrates, the temporal evolutions of the radial extension of the droplet R(t) on the various Cu substrates and at 800K and 1000K are demonstrated in Fig. 4, respectively. (The result for 900K is in between those for 800K and 1000K, but it is not

FIG. 2. Phase diagram of nanometer-scale Sn-Cu alloys. The range of weight fraction of Cu in the alloy considered in this diagram is between 0.0 and 0.6. The lower (upper) curve represents the solidus (liquidus) temperature as a function of the weight fraction of Cu.

DOI: 10.5101/nml.v2i2.p60-67 http://www.nmletters.org
shown here.) In the present analysis, the radial extension $R(t)$ is derived from the contact area of the nearest slab of the drop atoms above the substrate surface. As shown in Fig. 4, at a common temperature, the fastest wetting kinetics of the Sn droplet is on Cu(110), while the slowest one is on Cu(100) and in between is on Cu(111), but the radial extensions tend to become steady at approximately equal times. The difference of wetting kinetics is simply attributed to the distinct planar crystalline structures on these surface planes. On the (110) plane, the FCC copper atoms are less closely packed than those packed on the (111) and (100) planes, so Cu atoms on this plane dissolve into the liquid drop and bind to Sn atoms to form a surface alloy in a larger area at a time than those on the other planes do. The quicker (slower) radial extension on (110) ((100)) plane, however, gives rise to a lesser (denser) density of Cu in the alloy film, so Cu atoms from deeper (shallower) planes of the Cu crystal will melt into the droplet to complete the spreading at the specific temperature. As a result, the wettings on these planes tend to become steady at equal times. The $R(t)$ curves in Fig. 4 also indicate that in the early stage of the reactive wetting, all the film radii grow with $t^{1/2}$ and they have become steady quite early before 300 ps. Furthermore, the $R(t)$ curves in Fig. 4 demonstrate a natural phenomenon that a higher temperature (meaning that the droplet has higher kinetic energy) leads to a quicker radius growth. However, on a specific surface plane, the radius growth tends to become steady at an earlier time instant when wetting is performed at a lower temperature, reflecting the fact that the droplet saturates in a less Cu content for a lower temperature. In addition, as the radial extension comes to the end, a larger final radius also implies a smaller final contact angle. In this study, the final contact angle was simply approximated by calculating the formula $\theta_f = \arctan(h/R)$, where $h$ represents the height of the final film. The final contact angles of all Sn droplet wetting simulations performed in this work are listed in the first data row in Table 1. As shown, among all of the present simulations, the highest wettability is achieved when Sn wets the Cu(110) surface at 1000K, since the final contact angle in this case is the smallest.

The results shown in Figs. 4 lead to the conclusion that the 300 ps simulation time used in all the simulations performed herein is in fact sufficiently long, and the ending of all the wettings is thus designated to be at 300 ps. The Sn droplet wets the various Cu substrates with different speeds, but all the wettings should cease when the droplet saturates in Cu atoms; the latter phenomenon, however, should depend only on the temperature. To discuss the driving mechanism of the reactive

### Table 1. The final contact angles obtained in all the simulations performed in this work.

| Temperature | Surface   | 1000K       | 900K       | 800K       |
|-------------|-----------|-------------|------------|------------|
|             | Cu(100)   | Cu(111)     | Cu(110)    | Cu(100)    | Cu(111)    | Cu(110)    | Cu(100)    | Cu(111)    | Cu(110)    |
| 100wt%Sn    | 28.56     | 25.77       | 20.15      | 34.07      | 29.25      | 25.92      | 40.95      | 34.45      | 31.57      |
| Sn-10wt%Cu  | 29.61     | 27.48       | 24.41      | 34.10      | 32.40      | 28.28      | 41.80      | 35.20      | 34.9       |
| Sn-20wt%Cu  | 32.01     | 29.52       | 24.88      | 35.83      | 32.26      | 29.83      | 42.53      | 37.76      | 35.11      |
| Sn-30wt%Cu  | 32.63     | 29.55       | 25.80      | 36.82      | 32.38      | 30.5       | NA         | NA         | NA         |

DOI: 10.5101/nml.v2i2.p60-67 http://www.nmlett.org
wetting in more details, the density profiles for Cu and Sn in the wettings of the various surfaces by the pure Sn at 1000 K as functions of z after 300 ps are demonstrated in Fig. 5, as an example for depiction. The density function was calculated as an average over a circular region with radius 25 Å in x-y plane and with its center positioned at z axis. As demonstrated in Fig. 5, the crossover of the density profiles for both Cu and Sn around the substrate surface (z=0) clearly displays the inter-diffusion of these atoms occurring near the substrate surface during the wetting process. The domain where such crossover occurs thus is termed the inter-diffusion zone, or surface alloy zone. The density profiles for Cu in Fig. 5 show that, while Cu atoms of deeper planes remain intact, as reflected by the same density peaks on these planes, the upper planes of Cu in the crystal have decreased peak peaks of density, indicating that more Cu atoms on upper planes in part have melted into the liquid film. The reactive wetting of Cu(110) ((100)) achieves the thickest (thinnest) surface alloy layer. As shown, eleven (110) planes, five (111) planes, and only two (100) plans have decreased density peaks for Cu in the substrates, respectively. In the same time, Sn atoms have diffused into the Cu lattice; Sn can even be seen in the eighth (110) plane but only in the second (100) plane under the substrate surface. Several coexisting density peaks for Cu and Sn in the spreading film (z>0) also are found in the zone nearest to the substrate surface, implying the planar crystalline structure of the Sn-Cu alloy in this zone. In the spreading film, owing to the dissolution of Cu into the liquid, if Cu increases to some limit, depending on the specific temperature of the wetting system, then the Sn-Cu alloy will first become liquidus, i.e., the binary alloy is in liquid and solid phases simultaneously. Further increase of Cu content will cause the Sn-Cu binary composition to reach another limit, so the specific system temperature will become the solidus temperature of the alloy at which the Sn-Cu alloy will be solidified to its crystalline structure. The descending density peaks for Cu along z axis in Fig. 5 reveal that the solidification of the Sn-Cu alloy in the droplet is localized in the zone nearest to the substrate surface and the liquidus binary alloy is located above this zone. In this work, the theoretical boarder separating the solidus and liquidus binary alloys is defined as the liquid/solid interface of the surface alloy. During the wetting process, the zone of crystalline binary alloy will extend up into the spreading droplet, or, the liquid/solid interface will move upwards. Specifically, Webb III et al. have hypothesized that the reactive wetting of metallic droplet and substrate will proceed until the liquid droplet saturates in substrate atoms. In this work, the hypothesis is expressed as the reactive wetting proceeds until the liquid/solid interface stops moving upwards, while saturating with the solidus weight fraction of the substrate atom. However, a sharp liquid/solid interface in fact is not distinguishable; the density profiles in Fig. 5 cannot help identifying the liquid/solid interface precisely. This work thus presents a simple theory for positioning the theoretical liquid/solid interface, which should utilize the temperature-dependent solidus weight fraction of Cu in the Sn-Cu binary system, $W_\text{S}^{Cu}(T)$, as shown in Fig. 2. To determine the position of the liquid/solid interface, density peaks for Cu in the inter-diffusion zone are first used for curve-fitting a continuous density function, viz., $W_c(z)$. Then the liquid/solid interface of the surface alloy is defined to be located at $z=\text{zn}^\text{int}$ such that the second order differential derivative of the density function with respect to z vanishes, i.e., $d^2pc(z)/(dz^2)=0$, because the density for Cu at that point will be steady (i.e. time-independent) whereas the interface stops moving upwards, if the continuum model of mass diffusion is applied. Meanwhile, for each of the planes of atoms in the inter-diffusion zone, the density peaks for Cu and Sn of the plane are used for calculating the average weight fraction of Cu in the Sn-Cu binary system on the plane. At $z=\text{zn}^\text{int}$, the weight fraction of Cu in the binary alloy, denoted by $W_c^\text{Cu}(\text{zn}^\text{int})$, can be simply determined as the linear interpolation of the values at the two neighboring points that $\text{zn}^\text{int}$ is in between. The diagrammatic depiction of the determinations of $\text{zn}^\text{int}$ and $W_c^\text{Cu}(\text{zn}^\text{int})$ in the wetting of Cu(100) by Sn droplet at 1000K can be found in Fig.6, only for instance. During the spreading process, the position of the liquid/solid interface $\text{zn}^\text{int}$ will move upwards and the weight fraction $W_c^\text{Cu}(\text{zn}^\text{int})$ will increase with time as Cu atoms from the crystal keep melting into the droplet. The hypothesis presented here is that at a specific temperature T, the reactive wetting of Cu substrate by Sn or Sn-Cu alloys will come to the end when the liquid/solid interface stops at the final position $\text{zn}^\text{int}$ and saturates with Cu, i.e., $W_c^\text{Cu}(\text{zn}^\text{int})=W_c^\text{Sn}^{Cu}(T)$. Diagrammatic depiction of the movement of the liquid/solid interface for the wetting on Cu(100) plane performed at 1000K is demonstrated in the inset of Fig. 6. The black solid curves in Fig. 4 and the inset of Fig. 6 exhibit that both the growth of the spreading film’s radius and the movement of the liquid/solid interface become steady at the same time. The weight fraction $W_c^\text{Cu}(T)$ is dependent only on temperature and independent of the crystalline direction of the Cu substrate surface that the droplet wets. The results of all Sn wettings listed in the first data row of Table 2 have verified the correctness of the present

DOI: 10.5101/nml.v212.p60-67 http://www.nmletters.org
The fastest spreading hat, when performed at a specific
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The density profiles for Cu and Sn mentioned above are
dependent functions, which is very
symmetric. The plane
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-diffusion zone in fact is more likely two-dimensional (axially symmetric). Displayed in Fig. 7 are, in color scale, the
distributions of W
Cu
on several planes perpendicular to z axis
for the wettings of Cu(100) performed at 1000K; as shown in
the figure, the distributions are approximately axially
symmetric. The planes considered in Fig. 7 are the nearest
layers to the substrate surface and are positioned at which the
density peaks for Cu shown in Fig. 5 occur, including the first
two layers above (at z=z
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and z=z
2
) and under the substrate
surface (at z=z
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and z=z
2
), respectively. Figure 7 clearly shows
that, on the layers under the substrate surface, weight fraction of
Cu in the region nearer to z axis is smaller, indicating that
majorities of the Cu and Sn atoms that have melted into the
liquid and incorporated into the crystal, respectively, come from
this region. In contrast to these layers, on the layers above the
substrate surface diluter content of Cu is also observed in the
region nearer to z axis. In this work, on a plane the region
around z axis, where the weight fraction of Cu is relatively
small, is called the core zone of the plane. As shown in Fig. 7,
both liquid and solid alloys co-exist on the layer positioned at z
2
, which is above the theoretical liquid/solid interface, while only
solid alloys exist on the layer positioned at z
1
, which instead is
under the liquid/solid interface. Interestingly, on the plane z
2
, the
liquid alloys (with smaller W
Cu
) in the core zone are
surrounded by the solid alloys (with larger W
Cu
). The
distributions of weight fraction of Cu demonstrated in Fig. 7
depict that when substrate Cu atoms, especially those in the
core zone, followed by the Cu atoms from lower layers, face the
liquid they will melt into it. The Cu atoms in the liquid then will
diffuse outwards to the edge of the spreading film and finally,
together with Sn atoms, adhere to the underlying solid, causing
larger W
Cu
in region farther from the core zone. Near the end of
the spreading, only Cu atoms in the core zone, if still
unsaturated, will melt into the liquid. The present evidence
shows the liquid/solid interface is theoretically positioned in

hypothesis and the usability of the present theory. The results
listed in Table 2 reveal that, when performed at a specific
temperature T, wettings on the various substrates considered
herein have approximately a common W
Cu
(T), which is very
close to W
8
Cu
(T). Effects of the crystalline direction of Cu
surface only lead to different wetting kinetics and different
positions of the liquid/solid interface. At a common temperature,
the wetting on (110) plane gives the upmost final position of the
liquid/solid interface and that on (100) plane, the lowest
position, simply because the former has the fastest spreading
kinetics and the latter, the slowest.

The density profiles for Cu and Sn mentioned above are
averages over the circular region with radius 25 Å in x-y
plane and thus are simply expressed as z-dependent functions,
and so is the z-dependent weight fraction of Cu. Nevertheless,
the distribution of the weight fraction of Cu in the
inter-diffusion zone in fact is more likely two-dimensional
(axially symmetric). Displayed in Fig. 7 are, in color scale, the
distributions of W
Cu
on several planes perpendicular to z axis
for the wettings of Cu(100) performed at 1000K; as shown in
the figure, the distributions are approximately axially
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unsaturated, will melt into the liquid. The present evidence
shows the liquid/solid interface is theoretically positioned in

DOI: 10.5101/nml.v2i2.p60-67 http://www.nmletters.org
Table 2. The final positions of liquid/solid interface, $z_{int}$ (Å), and the corresponding weight fractions of Cu at the interface, $W^{Cu}(z_{int})$, in all the wettings simulated in this work.

| Temperature | 1000K | 900K | 800K |
|-------------|-------|------|------|
| Droplet     | Cu(100) | Cu(111) | Cu(110) | Cu(100) | Cu(111) | Cu(110) | Cu(100) | Cu(111) | Cu(110) |
| 100wt%Sn    | 0.80 (0.567) | 1.25 (0.567) | 1.30 (0.558) | 1.20 (0.519) | 1.45 (0.515) | 1.88 (0.512) | 1.42 (0.450) | 1.88 (0.450) | 1.90 (0.451) |
| Sn-10wt%Cu  | 0.83 (0.562) | 1.27 (0.562) | 1.35 (0.562) | 1.45 (0.520) | 1.60 (0.510) | 1.92 (0.509) | 1.70 (0.452) | 2.05 (0.452) | 2.15 (0.450) |
| Sn-20wt%Cu  | 0.87 (0.566) | 1.71 (0.564) | 1.90 (0.560) | 1.50 (0.520) | 1.90 (0.516) | 1.95 (0.508) | 1.78 (0.456) | 2.08 (0.456) | 2.20 (0.453) |
| Sn-30wt%Cu  | 1.20 (0.572) | 1.80 (0.565) | 1.97 (0.566) | 1.80 (0.520) | 2.03 (0.518) | 2.10 (0.514) | NA | NA | NA |

Average ± deviation: 0.56 ± 0.003 for 1000K, 0.515 ± 0.004 for 900K, and 0.452 ± 0.002 for 800K, respectively. These data are very close to the temperature-dependent solidus weight fractions $W_{Cu}(1000K)=0.562$, $W_{Cu}(900K)=0.515$, and $W_{Cu}(800K)=0.457$, respectively.

Data shown here exhibits that $W^{Cu}(z_{int})$ depends only on temperature. Average and deviation of the temperature-dependent $W^{Cu}(z_{int})$ are 0.564±0.003, 0.515±0.004, and 0.452±0.002 for 1000K, 900K, and 800K, respectively. These data are very close to the temperature-dependent solidus weight fractions $W_{Cu}(1000K)=0.562$, $W_{Cu}(900K)=0.515$, and $W_{Cu}(800K)=0.457$, respectively.

FIG. 7. Cross-section snapshots at 300 ps showing color scaled distributions of weight fraction of Cu on planes perpendicular to z axis for the wettings of Cu(100) at 1000K. The planes considered here are at (a) $z_1$=1.965 Å; (b) $z_2$=0.621 Å; (c) $z_3$=2.103 Å; and (d) $z_4$=4.051 Å, respectively. Inside the broken circle in each diagram is the area over which the densities of Cu and Sn are averaged.

between the planes $z_1$ and $z_2$. Under the interface, the core zone of plane $z_1$ is in solid phase and above it, the core zone of plane $z_2$ is still in liquid phase. Obviously, the melting of Cu into the liquid stops when the core zone of the theoretical interface is saturated with the solidus weight fraction $W_{Cu}^{solidus}$.

Figure 8 shows the influence of droplet composition on the radial extension R(t); a richer Cu content in the alloy droplet results in a slower wetting kinetics, the same trend as in the case of wetting by Cu-Ag alloys [22]. However, radial extensions in the wettings by the alloys in different compositions require approximately equal time to become steady. This is simply due to that, during the reactive wetting by a richer (diluter) Cu content droplet, fewer (more) Cu atoms are required to melt into the droplet to cause its saturation with Cu. Similar to the wettings by Sn, the time required for the radius growth in the Sn-Cu wettings to become steady is almost independent of the crystalline direction of the substrate surface.

The final contact angles of the wettings of the various Sn-Cu droplets performed at the various temperatures considered in this work are also listed in Table 1. This table depicts that the contact angle decreases with the decrease of Cu content for the Sn-rich Cu-Sn alloys, qualitatively consistent with the macroscopic observations of Amore et al. [6]. The hypothesis and theory described above can also be applied to the wettings by Sn-Cu alloy droplets. In the cases of the Sn-Cu droplet wettings, the final positions of the liquid/solid interface $z_{int}$ and the corresponding values of $W^{Cu}(z_{int})$ were obtained following the same procedure mentioned above. The results are listed in Table 2. Again, the hypothesis presented in this work is verified by the fact that, at a common temperature T, the weight fractions of Cu at the liquid/solid interfaces $W_{Cu}(z_{int})$ have approximately the same value of $W_{Cu}(T)$ for the wettings of the various alloy droplets. However, a richer Cu content in the binary alloy droplet results in an upper position of the liquid/solid interface.

In this work, a total of 36 MD calculations for simulating

FIG. 8. Variations of radius, R(t), for the spreading films of Sn (solid curves), Sn-10Cu (long dashed curves), Sn-20Cu (short dashed curves), and Sn-30Cu (dotted curves) on Cu(100) (black curves) and Cu(110) (red curves), respectively. Presented here are the results from the wettings performed at 1000K. The influence of the droplet’s alloy composition at other temperatures is similar to what is shown here.
reactive wettings of Sn/Cu systems have been performed. Reactive wettings of Cu(100), Cu(110), and Cu(111) substrates by pure Sn and Sn-10Cu, Sn-20Cu, and Sn-30Cu(wt%) alloy droplets at the temperatures of 800K, 900K, and 1000K were considered, respectively. The simulation results show that the spreading of Cu(110)/(Cu(100)) substrate has the fastest (slowest) wetting kinetics and the highest (lowest) final position of the theoretical liquid/solid interface separating the liquidus and solidus Sn-Cu alloys in the surface alloy film. Wettings performed at a higher temperature also have faster kinetics but require longer times to become steady. A higher temperature will lower the position of the liquid/solid interface in the surface alloy. Meanwhile, the influence of the droplet’s alloy composition is that a richer Cu content causes the alloy droplet to wet the substrates with a slower kinetics and a lower position of the liquid/solid interface. This work considered the regime where the dissolution of the substrate Cu into the liquid dominates the reactive wetting. A hypothesis that the reactive wetting will come to the end as the theoretical liquid/solid interface saturates with the temperature-dependent solidus Sn weight fraction of Cu and stops moving into the droplet has been confirmed through a theory successfully developed in this work for positioning the liquid/solid interface in the spreading film. However, the realistic distribution of the weight fraction of Cu in the surface alloy is axially symmetric. In the region farther from the z axis richer contents of Cu are observed both in the alloys above and under the substrate surface, reflecting less amount of Cu in the crystal have melted into the liquid droplet and the Cu atom that have melted into the droplet tend to diffuse to the edge of the liquid film. In the zone of coexisting liquid and solid alloys, the liquid alloy is surrounded by the solid alloy. Summarized, this work has presented detail knowledge of the reactive wetting of Sn/Cu systems, which is necessarily required in relevant lead free soldering processes.

Received 11 March 2010; accepted 1 April 2010; published online 22 April 2010.

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The model developed for stress-induced structural phase transformations of micro-crystalline silicon films

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The nanoindentations were applied to island-shaped regions with metal-induced Si crystallizations. The experimental stress-strain relationship is obtained from the load-depth profile in order to investigate the critical stresses arising at various phase transitions. The stress and strain values at various indentation depths are applied to determine the Gibbs free energy at various phases. The intersections of the Gibbs free energy lines are used to determine the possible paths of phase transitions arising at various indentation depths. All the critical contact stresses corresponding to the various phase transitions at four annealing temperatures were found to be consistent with the experimental results.

Keywords: Silicon films; Phase transitions; Stress-strain model

Citation: Chang-Fu Han and Jen-Fin Lin, “The model developed for stress-induced structural phase transformations of micro-crystalline silicon films”, Nano-Micro Lett. 2, 68-73 (2010). doi: 10.5101/nml.v2i2.p68-73

The depth-sensing indentation (nanoindentation) test is a powerful tool for determining the mechanical properties of bulk specimens [1-6] and thin film/substrate systems [7-9]. Atomistic simulations of nanoindentation have been performed to investigate anisotropic effects in elastic and incipient plastic behavior under nanoindentation [10-12]. The determination of atomistic fracture modes under various loading conditions is essential to understanding nanomechanics. Pan et al. [13] reported first-principles calculations that show intriguing indenter-angle-sensitive fracture modes and stress responses at the incipient plasticity of strong covalent solids. A basic micromechanical model for the deformation of solids with only one tuning parameter has been introduced. The model can reproduce observed stress-strain curves, acoustic emissions and related power spectra, event statistics, and geometrical properties of slip, with a continuous phase transition from brittle to ductile behavior [14-16]. Nanometer scale indents have been written in a cross-linked polystyrene sample, and their relaxation has been studied at annealing temperatures well below the glass transition of the polymer [17]. The indentation stress-strain curve exhibits a series of yielding events, attributed to the nucleation and movement of dislocations [18]. In porous silicon [19], a transition from the diamond phase to a high density amorphous (HDA) phase has been reported. Nanocrystalline silicon [20] undergoes a direct transition from diamond to a simple hexagonal structure. One such prediction was a kinetically hindered first order amorphous to amorphous phase transition in SiO₂ [21]. An experiment has recently confirmed such a first order amorphous to amorphous phase transition [22]. Such calculations require candidate structures which may be obtained from constant pressure simulations and sometimes experiments [23,24]. In the present study, a theoretical model is developed

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using contact stress-strain analysis and Gibbs free energy to investigate the stress-induced phase transitions arising at various nanoindentation depths of microcrystalline silicon (µc-Si). Four kinds of Al/a-Si/Glass 7740 specimen with silicon crystallizations were prepared at four annealing temperatures (350°C, 400°C, 450°C, and 500°C), respectively. The Al film was then removed by wet etching. A model with originality is developed in order to transform the experimental load-depth results into stress-strain relationships. The stress-strain results allow us to calculate the values of Gibbs free energy for the possible phases arising at various indentation depths. The intersection points of these Gibbs free energy lines can be used to determine the possible paths of phase transitions.

Stress Analyses of Composite Film

During the indentation test, the composite film layer may delaminate from its substrate if the indentation depth, thus the indentation load, is sufficiently high. The deformation of the composite film under a uniform pressure distribution can thus be imagined as the deflection of a membrane. From the bending assuming elastic deformation, the internal stress $\sigma$ created in the undeformed composite film with a thickness of $t$. The internal stress $\sigma$ and the contact force $F_c$ satisfy the following relation [25-26]:

$$\sigma_I = \frac{F_c}{12\sqrt{3} \cdot h \cdot t},$$

(1)

The values of $F_c$ and $h_c$ can be obtained from the load(P)-depth(h) analyses of the nanoindentation test [26,27]. The contact depth, $h_c$, can be obtained using the method of Oliver and Pharr [2]. Recent experiments have revealed that the results of nanoindentation strongly depend on indenter geometry [28-30]. Here, we examine the atomic response to nanoindentation by a sharp indenter with various centerline-to-face angles $\alpha$. From the stress response to incipient plasticity developed by Pan et al. [13], the contact stress $\sigma_c$ and indentation strain $\varepsilon_c$ in Fig. 1 are related by:

$$\frac{\sigma_c}{\sigma_I} = \frac{\varepsilon_c}{\varepsilon_I} = \tan \alpha$$

(2)

$\sigma_c$ can be obtained from the above equation since the angle $\alpha$ is known. The application of contact stress to solids leads to a diverse collection of interesting phenomena. The most dramatic behavior may be the stress-induced phase transitions. Stress-induced phase transitions in microcrystalline silicon (µc-Si) have been extensively studied [19-24]. In order to study the model of crystallization, the volume-dependent Gibbs free energy is evaluated. To calculate the static structural properties of the silicon phase, the total energy $E_{\text{tot}}$ can be obtained in a polynomial form, expressed as Murnaghan’s equation of state [31]:

$$E_{\text{tot}}(V) = \frac{B_V}{B'(B' - 1)} \left( \left[ \frac{V}{V_m} \right]^3 - 1 \right) + E_{\text{m}}$$

(3)

and

$$V_i = \frac{V}{V_m}$$

(4)

where $V$ and $V_i$ are the volume and transition volume per atom at various phases of silicon, respectively. $V_{\text{min}}$ is the volume per atom corresponding to the minimum total energy $E_{\text{min}}$ per atom. The crystal data at diamond-Si, body-centered tetragonal (β-tin Si), primitive hexagonal (ph-Si), and HDA phases of silicon includes $V_{(\text{diamond-Si})}=0.89$, $V_{(\beta\text{-tin Si})}=0.71$, $V_{(ph\text{-Si})}=0.69$, $V_{(HDA)}=0.65$, $V_{\text{min}}(\text{diamond-Si})=20.76$ Å$^3$, $V_{\text{min}}(\beta\text{-tin Si})=15.42$ Å$^3$, $V_{\text{min}}(ph\text{-Si})=15.66$ Å$^3$, $V_{\text{min}}(HDA)=15.87$ Å$^3$, $E_{\text{m}}(\text{diamond-Si})=-108.00$ eV, $E_{\text{m}}(\beta\text{-tin Si})=-107.71$ eV, $E_{\text{m}}(ph\text{-Si})=-107.68$ eV, and $E_{\text{m}}(HDA)=-107.53$ eV, as obtained from the studies in [23,24,31]. In the present study, $B_0$ and $B'$ are the bulk modulus and the pressure derivative of the bulk modulus for silicon with $V_{\text{min}}$, respectively. This study calculates the indentation stress based on the thermodynamics theorem. When a transition occurs, the Gibbs free energy at zero temperature between the two phases is the same. The Gibbs free energy is written as:

$$G = E_{\text{tot}} + \sigma_c V$$

(5)

The contact stresses corresponding to these phase transitions can be evaluated from Eq. (5) if the Gibbs free energy ($G$) and the total energy ($E_{\text{tot}}(V)$ in Eq. (3)) are available. These stresses predicted by the proposed model are compared with the experimental results in order to validate the proposed model for the prediction of phase transition.

DOI: 10.5101/nml.v2i2.p68-73
Results and Discussions

The indentation tests were carried out on a Nano Indenter XP (MTS, USA) tester. All experiments were carried out using the Berkovich indenter, which was made of diamond (Young’s modulus \( E = 1140 \text{ GPa} \), Poisson’s ratio \( \nu = 0.07 \)). In this study, the substrates used for the aluminium (Al)/amorphous silicon (a-Si) structure were made of Corning glass (code 7740). a-Si films with a thickness of 200 nm were deposited onto the glass substrate using an ultra-high vacuum ion beam sputtering system (UHV-IBS, model IBS-2000 ULVAC, Japan) with a high purity target of Si (99.999%). An Al layer with a thickness of 50 nm was thermally evaporated and deposited onto the a-Si layer. When the aluminum depositions were finished, the glass was cut into small pieces and annealed at temperatures of 350°C, 400°C, 450°C, and 500°C respectively. The remaining Al was then removed by wet selective etching after the annealing process. The microstructure was characterized using focused ion beam microscopy (FIB, FEI Nova-200 NanoLab compatible, USA) and high-resolution transmission electron microscope (HR-TEM, JEM-2100F, JEOL, Japan) was used to investigate the density of Si crystallization. In the present study, the Al (50 nm)/a-Si (200 nm)/Glass 7740 (substrate) specimens were treated at four annealing temperatures and at room temperature (25°C). No silicon crystallization was found at the a-Si layer for the specimen that was prepared without further annealing (at room temperature), as shown in Fig. 2(a). However, Si crystallizations appear as grains with various sizes at the a-Si layer for annealing temperatures \((T)_{\text{annealing}} \geq 350 \text{°C}\). This specimen was annealed at a temperature of 350°C as shown in Fig. 2(b). In this figure, many black island-shaped stains can be seen on the annealed Si layer.

Figure 3(a) shows the cross section of the nanoindentation applied at a stain in Fig. 2(b) with silicon crystallizations. The white dashed lines enclose the final indentation cavity. There is a dark band surrounding the cavity. Point B in Fig. 3(b) is exactly beneath the cavity tip. Point A is considerably far from the boundary of the indentation cavity, but is still in the region of Si crystallization. Point C is exactly beneath the cavity tip and near the interface of the (a-Si+µc-Si) film layer and the Glass 7740 substrate, but still at the (a-Si+µc-Si) film layer. Point D is located beneath point C; it is at the protrusion of the Si-layer into the region originally belonging to the Glass 7740 substrate. The TEM diffraction pattern in the bottom-left corner shows point A being induced to the primitive hexagonal silicon phase by the contact stress \( (\sigma_c) \). The TEM diffraction pattern for point B is shown in the bottom-right corner of Fig. 3(c); it was identified as the HDA Si phase [20]. The TEM diffraction pattern of the phases shown in Fig. 3(d) for point C and point D were identified as largely the amorphous phase, even though very little crystalline behavior is still existent. Therefore point C and point D are located in the region affected by the stress-induced crystallizations. The coexistence of the amorphous and crystalline regions in the (a-Si+µc-Si) film layer near the indentation cavity confirms the validity of the phase transitions predicted by the proposed model.

Figure 4(a) shows the \( \sigma_c - \varepsilon_c \) curve of the Al/a-Si/Glass 7740 specimen annealed at 350°C after nanoindentation obtained from the proposed model. The non-smooth curve indicates that stress-induced phase transitions occurred at various critical stresses \( (\sigma_{\text{c},i} = 1,2,3\ldots) \). The possible phases are identified as diamond cubic Si, the body-centered tetragonal \((\beta\text{-Si})\), the primitive hexagonal Si \((p\text{-Si})\), and HDA Si phases [23,24,31]. Figure 4(b) shows the four lines of Gibbs free energy corresponding to the four possible phases of silicon as a function of \( \sigma_c \). As Fig. 4(b) shows, the specimen begins with the diamond Si phase; the \( G_{\text{diamond-Si}} \) line intersects the \( G_{\beta\text{-Si}} \) line at the point where \( \sigma_c=6.04 \text{ GPa} \). The \( \sigma_c \) value is defined as the dashed line of \( \sigma_{\text{c},i} \) in Fig. 4(a). After this point, an increase in the indentation depth, and thus the \( \sigma_c \) value, allows the Si layer to operate in the \( \beta\text{-Si} \) phase, which is indicated by the arrow on the \( G_{\beta\text{-Si}} \) line. When the \( \sigma_c \) value increases to 8.65 GPa, the \( G_{\beta\text{-Si}} \) line intersects the \( G_{p\text{-Si}} \) line. Therefore, the \( \beta\text{-Si} \) phase transforms to the primitive hexagonal phase \((p\text{-Si})\) if the \( \sigma_c \) value is higher than 8.65 GPa. This value is here defined as \( \sigma_{\text{c},3} \). As Fig. 4(b) shows, the diamond Si phase can also directly transform into the HDA Si phase. The critical contact stress corresponding to this direct transition is 8.82 GPa. Figure 4(c) shows the Raman spectra for the specimens annealed at 350°C before and after nanoindentations, respectively. In the specimen before nanoindentation, the sole intensity peak appears at 518 cm\(^{-1}\). This peak in the Raman band is identified as the diamond cubic (Si-I) phase. For the Raman bands in the cavity after nanoindentation, peaks at 518 cm\(^{-1}\), 476 cm\(^{-1}\), 446 cm\(^{-1}\), 403 cm\(^{-1}\), and 357 cm\(^{-1}\) were observed in the specimen. The Raman bands at 357 cm\(^{-1}\) and 446 cm\(^{-1}\) were identified as the rhombohedra \((r8)\) Si-II phase and the body-center-cubic \((bc8)\) Si-III phase, respectively [29,32-35]. These two phases appeared in the unloading process of nanoindentation only. The peaks corresponding to 403 cm\(^{-1}\), 476 cm\(^{-1}\), and 518 cm\(^{-1}\) are the three phases in the loading process. The peak at 403 cm\(^{-1}\) was identified as the body-centered tetragonal \((\beta\text{-Si})\) Si-II and primitive
hexagonal (ph-Si) Si-V phases [36]. The peak at 476 cm$^{-1}$ was identified as the amorphous and HDA phases [34]. This phase was created due to the stress-induced phase transition shown at one of the two predicted paths shown in Fig. 4(b). Figure 4(d) shows the experimental $\sigma_c - \varepsilon_c$ results for the five specimens treated at four annealing temperatures and with no annealing, respectively. The dashed curves denoted by $\sigma_{c1}$ and $\sigma_{c3}$ were obtained from the predictions of the proposed model. These dashed curves intersect the $\sigma_c - \varepsilon_c$ curves at the points symbolized by “▲”. It was found that the intersection points

FIG. 2. Surface image of the Al (50 nm)/a-Si (200 nm)/Glass 7740 specimen at room temperature (25°C). (b) Morphology of the Si layer after etching of the Al layer at an annealing temperature of 350°C.

FIG. 3. Bright field HR-TEM micrographs of (a) the cross-section after indentation, (b) the local magnification of the indentation cavity and the diffraction pattern of point A, (c) the diffraction pattern of point B, and (d) the diffraction pattern of point C and point D.

DOI: 10.5101/nml.v2i2.p68-73 http://www.nmletters.org
are very close to the two turning points of the $\sigma_c - \varepsilon_c$ curve, respectively, for each of the four curves for annealed specimens. Therefore, the predictions by the proposed model are effective for all the specimens with phase transitions.

**Conclusion**

The contact stress ($\sigma_c$) and contact strain ($\varepsilon_c$) models developed in the present study for nanoindentations allow us to obtain the experimental $\sigma_c - \varepsilon_c$ curve and thus identify the critical values for stress-induced phase transitions at various indentation depths. The contact stress and contact strain developed in the proposed model are provided to determine the Gibbs free energy for various phases. The critical contact stresses corresponding to phase transitions can be determined from the intersections of the Gibbs free energy lines. Then, the paths from the start of diamond cubic silicon to the possible final phases corresponding to the maximum indentation depth can be identified. The theoretical predictions of final phases in the present study were confirmed by TEM diffraction patterns and Raman spectra.

This work has been granted by Frontier Materials and Micro/Nano Science and Technology Center, National Cheng Kung University, Taiwan, R.O.C.

Received 10 March 2010; accepted 15 April 2010; published online 22 April 2010.

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Identification of binding interactions between myeloperoxidase and its antibody using SERS

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Surface Enhanced Raman Spectroscopy (SERS) is a widely used spectroscopic method that can dramatically increase the sensitivity of Raman spectroscopy and has demonstrated significant benefit in the identification of biological molecules. We report the use of SERS in differentiating the bound immunocomplex of myeloperoxidase (MPO) and its antibody from the unbound complex and its individual components. The SERS signal was enabled by gold nanoparticles attached to MPO, pAb and their immunocomplex at an excitation wavelength of 785 nm. The obtained SERS spectrum of MPO is in agreement with previous literature. Comparative SERS spectrum analysis of MPO, pAb, and their immunocomplex reveals the significant peak shifts and intensity variations caused by the conformational changes due to the immunocomplex formation. Several key areas have been identified which correspond to specific amino acids being shielded from undergoing resonance while new amino acid residues are made visible in the SERS spectrum of the immunocomplex and could be a result of conformational binding. Our work demonstrates the capability of SERS to identify binding events and differentiate an immunocomplex from its unbound components with direct applications in biosensors.

Keywords: Gold nanoparticle; Antigen; Immunocomplex; Biosensors

Citation: E. S. Papazoglou, S. Babu, S. Mohapatra, D. R. Hansberry and C. Patel, “Identification of binding interactions between myeloperoxidase and its antibody using SERS”, Nano-Micro Lett. 2, 74-81 (2010). doi:10.5101/nml.v2i2.p74-82

Raman spectroscopy is a useful technique, based on Raman scattering, that has been widely used for molecular material characterization. When the electric field of a monochromatic light source (laser) interacts with a molecule it induces a dipole moment and causes the molecule to deform. The oscillatory nature of the laser beam’s electric field causes periodic changes in the dipole moment resulting in vibration of the molecule which are characteristic of the molecule under investigation. The interaction of the molecule with a photon results in the molecule, either losing one vibrational quantum of energy or gaining one vibrational quantum of energy, and this is referred to as Stokes Raman scattering or anti-Stokes Raman scattering, respectively. Raman spectroscopy most commonly measures vibrational energy states but can also measure rotational or electronic energy states. The main challenge of Raman spectroscopy has been the difficulty in separating the weak inelastic Raman scattering signal from the overwhelmingly dominant elastic Rayleigh scattering. For every photon that undergoes Raman scattering there are at least 10 million photons that undergo Rayleigh scattering.

Surface-enhanced Raman spectroscopy (SERS) provides a solution to this challenge by enhancing the signal intensity of Raman scattering of molecules adsorbed to roughened metal surfaces by as much as $10^{15}$ [1]. Fleischman et al. [2] was the first to note this enhanced effect in 1973 while observing the adsorption of pyridine on a silver electrode. Later two groups,
Jeanmarie et al. [3] and Albrecht et al. [4] independently realized this as a unique phenomenon and proposed both an electromagnetic mechanism and a chemical mechanism, as theoretical explanations for the enhanced signal. Gold and silver nanoparticles are commonly used as SERS substrates with gold particles being used more frequently due to their high sensitivity and stability compared to silver compounds [5-8]. It must be noted that the enhanced Raman signal enabled by the plasmon resonance of gold and silver nanoparticles gave rise to new biosensors that have been used for identifying the binding region in proteins [9], and for studying binding affinity of immunoreactions [10]. Signal analysis of SERS was used to identify the native constituents of live epithelial cells employing endocytosed 60 nm gold nanoparticles [11]. SERS has also been used to differentiate bacteria from bacteriophages by conjugating them to 60nm gold nanoparticles [12] and in single molecule detection [13,14]. The combination of plasmon resonance based sensing with real-time SERS analysis could become a novel tool for interrogating the dynamics of protein binding interactions.

Applications of SERS in immunosensing include the successful detection of the thyroid stimulating hormone (TSH) [15], monitoring the immunocomplex formation between mouse IgG and goat anti-mouse IgG [16], detection of membrane bound enzymes within cells and correlation of prostaglandin-H-synthase (PGHS) antigen levels [17], and detection of conformational binding of anti-mouse IgG (bound to gold nanoparticles of 29.7 nm diameter) to mouse IgG antigen [18].

Myeloperoxidase (MPO) is a lysosomal protein found in neutrophilic granulocytes, often overexpressed in inflammatory diseases [19-21]. MPO is a vital protein found in neutrophilic granulocytes that has an instrumental role in attacking bacteria and foreign pathogens. Neutrophilic granulocytes phagocytose pathogens and eliminate them through chemical reactions. MPO is capable of producing both hypochlorous acid and tyrosyl radicals in independent pathways. Hypochlorous acid and the tyrosyl radical are both cytotoxic and degrade bacteria and foreign pathogens. MPO is a 140kDa dimmer composed of two identical halves, each with a covalently bound heme and connected by a lone disulfide bond. In addition to the heme group located on each half of the MPO molecule there is a bound chloride group located on each half of the MPO molecule, and there is a bound chloride group located on each half of the MPO molecule. MPO contains two equivalent chlorine prosthetic groups.

To our knowledge Raman spectroscopic studies on MPO have been primarily performed using Resonance Raman Spectroscopy (RRS). RRS yields higher peak intensity compared to conventional Raman spectroscopy which translates to a lower sample concentration requirement. Our interest lies in using SERS to identify bands that are unique to the immunocomplex of MPO and its antibody and explore the use of such bands as signatures of binding events. In this paper, we report our results in differentiating the SERS signal of the MPO/pAb immunocomplex from the unbound complex and its individual components.

**EXPERIMENTAL METHODS**

All chemicals were purchased from Sigma Aldrich unless otherwise mentioned. pAb (rabbit anti human myeloperoxidase) was purchased from ABD-Serotec and myeloperoxidase (MPO) was purchased from Lee Biosolutions Inc.

Gold nanoparticles were prepared according to Frens, G. [24] with added modifications. 500µl of 1% chloroauric acid (HAuCl₄) were added to 50ml of distilled H₂O and heated to a boil under constant stirring. Upon boiling 400µl of 1% citric acid (C₆H₇O₆) were added. The size of nanoparticles could be controlled by varying the volume of citric acid being added; higher volume corresponds to smaller particles and lower volume corresponds to larger particles. 400µl of 1% citric acid correspond to 40nm particles. The solution was refluxed until the color was changed from dark blue to red. The solution was then removed from heat and allowed to cool to room temperature. The solution was further dialyzed in DI H₂O for 48 hours with the water being changed at 3, 12, and 24 hours, in order to remove citrate ions from the solution. Particle characterization was performed with UV-vis spectroscopy [25], atomic force microscopy, and scanning electron microscopy. Thus prepared gold nanoparticles were then immobilized on silane functionalized glass slides. Silanization of glass slides was achieved by the method followed by Park et al. [26]. In brief, glass slides were cleaned using piranha solution (1:3 v/v, H₂O₂:H₂SO₄) and dried under nitrogen. Cleaned glass slides were then immersed in 3% 3-aminopropyltrimethoxysilane (APTMS) in methanol for 3 hours. Silanized slides were then rinsed thoroughly with methanol followed by DI water and drying with a jet of dry nitrogen. Silanized glass slides were then immersed in the dialyzed gold nanoparticle solution for 3 hours. Slides with immobilized gold nanoparticles were then washed with DI water and air dried. A well with a capacity of ~100 mL was constructed using plastic pipette and epoxy on top of the glass slide to facilitate pAb immobilization and subsequent SERS data collection.

DOI: 10.5101/nml.v2i2.p74-82
Polyclonal antibody was immobilized by letting ~100 ml of 100 nM pAb solutions interact with the gold nanoparticle coated slides for 15 minutes at room temperature followed by thorough washing with 1x PBS buffer (pH7.4). Gold nanoparticles coated with pAb were then allowed to interact with MPO (100 μl, 1 μM) for 15 minutes at room temperature followed by washing. A similar procedure was followed to immobilize MPO (100 μl, 1 M) directly on gold nanoparticles. SERS data was collected from the Au-pAb conjugates, Au-pAb/MPO immunocomplex, and Au-MPO conjugates immediately after preparation using a Renishaw RM1000 confocal Raman microspectrometer with a 50x long focal microscope. A 785nm diode laser (15 mW) was used to collect the SERS signal. Care was taken to maintain a ~50 μl of PBS buffer to minimize thermal damage and the SERS data was collected from an area of ~40x40 μm square (~100 data points) located at the center of the well. SERS signal from glass slides coated with gold nanoparticles was also collected and served as the background signal.

Spectra with errors due to cosmic ray influence were removed manually resulting in an average of 75 spectra per sample. Individual spectra were then subjected to a three point baseline correction. The three points for baseline correction were kept the same for all spectra and samples, typically the first and last point corresponding to the beginning and end of the wave numbers of the spectra and the third point being set at 1369 cm⁻¹. This baseline correction applied to all data sets helped smooth the data and allow an appropriate comparison. Following the baseline correction individual spectra were normalized and averaged. In order to remove the gold nanoparticle (AuNp) signature from the spectra, the average AuNp spectrum set was subtracted from averaged spectra of Ab, MPO and MPO-pAb. The sum of Ab and MPO spectra was obtained by simply averaging the two spectra in Origin Pro. Origin 8.0’s peak analyzer module was used to fit peaks to the averaged spectra.

RESULTS AND DISCUSSION

Raw SERS spectra of AuNp, Ab, MPO, and MPO-pAb are shown in Fig. 1a-1d, respectively. Individual spectra in Fig. 1 were sorted by their average intensity for easy visualization. The background spectra i.e. spectra of AuNp (see Fig. 1a) reveal the typical fluorescence response of AuNp under experimental conditions [27]. Peak positions as well as peak width remain the same between various spots on the scanned area, demonstrating the reproducibility of the collected SERS data. Figure 1b-1d demonstrate the influence of the AuNp on the spectra of the pAb, MPO and MPO-pAb respectively. This necessitates removal of the AuNp interference from the rest of the dataset. Baseline corrected Ab, MPO and MPO-pAb spectra are shown in Fig. 2a, b and c, respectively. In order to identify spectral changes due to the binding of pAb and MPO as opposed to simple superposition...
we compared the spectra of AbMPO and the sum of spectra of pAb and MPO as shown in Fig. 3. Table 2 the peak positions of AbMPO along with the peaks that were found to be distinct for their immunocomplex. The peak positions that are unique for the immunocomplex are shown with the respective error bars (average of 80 spectra).

The SERS spectrum of MPO (see Fig. 2b) exhibits strong similarities to the Raman signals reported in previous studies [23,28-31]. It is relatively weak below 1100 cm\(^{-1}\), besides three small peaks between 646 cm\(^{-1}\) (\(\nu_{48}/\nu_{25}\)) to 684 cm\(^{-1}\) (\(\nu_{7}\)), at 835 cm\(^{-1}\), and between 992 cm\(^{-1}\) (\(\gamma(CH)\)) and 1007 cm\(^{-1}\) (\(\nu_{45}\)). Table 1 summarizes the MPO Raman peaks published by various studies. The minor peak assignments in our study are in excellent agreement with Zbylut S. D. et al., including the vibrational modes at \(\nu_{44} (1007 \text{ cm}^{-1})\), \(\gamma(CH) (992 \text{ cm}^{-1})\), \(\nu_{46} (925 \text{ cm}^{-1})\), \(\gamma_{10} (853 \text{ cm}^{-1})\), \(\gamma_{15} (710 \text{ cm}^{-1})\), \(\nu_{1} (684 \text{ cm}^{-1})\), and \(\nu_{46}/\nu_{25} (646 \text{ cm}^{-1})\) [32]. The MPO spectrum from 1120 cm\(^{-1}\) to 1260 cm\(^{-1}\) is also found to be similar to that previously published from resonance Raman spectra [31]. Notably there are significant peaks at 1137 cm\(^{-1}\) (\(\nu_{43}\)), 1214 cm\(^{-1}\) (\(\nu_{13}\)), and 1251 cm\(^{-1}\) (\(\nu_{2}\)). These peaks are consistent with previous literature on resonance Raman spectra of MPO [23,28-31]. Our work using a 785 nm excitation

FIG. 2. SERS spectra of averaged (a) Ab, (b) MPO, and (c) AbMPO cm\(^{-1}\), and between 992 cm\(^{-1}\) (\(\gamma(CH)\)) and 1007 cm\(^{-1}\) (\(\nu_{46}\)).

FIG. 3. Comparison of AbMPO spectra with sum of Ab and MPO spectra.
Table 1. Comparison of MPO Raman signal across multiple studies.

| vibrational mode | sym. | MPO\textsuperscript{**}a | MPO\textsuperscript{**}b | MPO\textsuperscript{**}c | MPO\textsuperscript{**}d | MPO\textsuperscript{**}e | MPO\textsuperscript{**}f | MPO\textsuperscript{**}g | MPO\textsuperscript{**}h | MPO\textsuperscript{**}i | MPO\textsuperscript{**}j | MPO\textsuperscript{**}k | MPO\textsuperscript{**}l |
|------------------|------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| v10              | B1g  | 1620 s               | 1608 s               | 1617                 | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    |
| v2 (C≡C)         | –    | 1615 s               | overlapped           | 1607                 | 1614                 | 1606                 | 1614                 | 1612                 | 1614                 | 1610                 | 1607                 | –                    | –                    |
| v37              | Eu   | 1595\textsubscript{i,k} | 1588                 | 1592                 | 1582                 | –                    | –                    | –                    | 1593                 | –                    | –                    | –                    | –                    |
| v2               | A1g  | 1590 s               | 1588 s               | 1568                 | 1587                 | –                    | –                    | –                    | 1585                 | 1587                 | 1576                 | 1585                 | 1586                 |
| v19              | A2g  | 1572                  | 1569 m               | 1564i                | –                    | 1561                 | –                    | –                    | –                    | –                    | –                    | –                    | –                    |
| v11              | B1g  | 1552 s               | 1548 m               | 1551                 | 1544                 | –                    | –                    | –                    | 1550                 | 1543                 | 1550                 | 1549                 | –                    |
| v38              | Eu   | 1531                 | 1525 m               | 1527i                | 1523                 | 1524                 | 1523                 | 1523                 | 1523                 | 1524                 | 1525                 | 1528                 | –                    |
| 2v15             | –    | 1509                 | 1505j                | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | 1504                 | –                    |
| v3               | A1g  | 1488                 | 1483 m               | 1470 m               | 1482                 | 1486                 | 1472                 | 1479                 | 1481                 | 1481                 | –                    | –                    | –                    |
| v28              | B2g  | 1474 l               | –                    | 1469                 | –                    | 1472                 | –                    | –                    | –                    | –                    | –                    | 1472                 | –                    |
| \(\delta (\text{C}=\text{H2})\) | –    | 1432                 | 1430 w               | 1425 w               | –                    | 1422                 | 1424                 | –                    | –                    | –                    | –                    | 1424                 | –                    |
| v40              | Eu   | 1396                 | 1401 sh              | –                    | 1396                 | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    |
| v20              | A2g  | 1387 i               | 1379 w               | 1378                 | –                    | –                    | –                    | –                    | –                    | –                    | –                    | 1386                 | –                    |
| v12              | B1g  | 1375 s               | 1362 sh              | –                    | 1378                 | –                    | –                    | –                    | 1377                 | –                    | 1376                 | 1377                 | –                    |
| v4               | A1g  | 1366 s               | 1352 s               | 1366                 | –                    | 1366                 | 1359                 | –                    | –                    | –                    | –                    | –                    | –                    |
| 2v7              | –    | 1362j                | –                    | 1351                 | –                    | 1359                 | 1363                 | 1363                 | 1363                 | 1362                 | 1355                 | –                    | –                    |
| v41              | Eu   | 1335                 | 1335 m               | 1331 w               | 1339                 | 1329                 | –                    | –                    | 1332                 | 1331                 | –                    | –                    | –                    |
| \(\delta (\text{CH=})\) | –    | 1326                 | 1320 sh              | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    |
| v21              | A2g  | 1305 m               | 1305 w               | 1307                 | 1306                 | –                    | –                    | –                    | 1307                 | 1307                 | 1306                 | –                    | –                    |
| CH2 wag          | –    | 1272                 | 1268 m               | 1267                 | 1267                 | –                    | –                    | –                    | –                    | –                    | 1265                 | 1265                 | –                    |
| v42              | Eu   | 1251                 | 1248 w               | 1242 m               | –                    | 1241                 | –                    | –                    | –                    | –                    | 1238                 | 1240                 | 1242                 |
| CH2 twist        | –    | 1223 w               | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    |
| v13              | B1g  | 1214                 | 1205 m               | 1205 m               | 1207                 | 1206                 | –                    | –                    | 1206                 | 1208                 | 1205                 | 1207                 | –                    |
| v30              | B2g  | 1169                 | 1173                 | 1156 vw              | 1161                 | –                    | –                    | –                    | –                    | 1163                 | 1162                 | –                    | –                    |
| v44              | Eu   | 1142 k               | –                    | –                    | 1139                 | 1116                 | 1116                 | –                    | –                    | –                    | –                    | –                    | –                    |
| v14              | B1g  | 1137                 | 1130 m               | 1137 w               | 1133                 | –                    | –                    | –                    | 1131                 | 1134                 | 1130                 | 1132                 | 1138                 |
| v5/v22           | A1g/A2g | 1112 m           | 1107 m               | 1114                 | 1107                 | –                    | –                    | –                    | 1111                 | 1111                 | 1110                 | 1106                 | 1107                 |
| \(\delta (\text{C}=\text{H2})_{\text{cm}}\) | –    | 1073                 | 1063 w               | –                    | 1068                 | –                    | –                    | –                    | –                    | 1069                 | 1068                 | –                    | –                    |
| v23              | A2g  | 1033 w               | 1029 vw              | 1034                 | 1026                 | –                    | –                    | –                    | 1034                 | 1029                 | 1027                 | –                    | –                    |
| v45              | Eu   | 1007                 | 998 m                | 984 w                | 1003                 | –                    | –                    | –                    | 1003                 | 1001                 | 1003                 | –                    | –                    |
| \(\gamma (\text{CH})\) | –    | 992                  | 985 w                | 984 w                | 979                  | 989                 | –                    | –                    | 984                  | 983                  | –                    | –                    | –                    |
| v46              | Eu   | 935 vw               | –                    | 934                  | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    |
| \(\gamma (\text{C}=\text{H2})_{\text{cm}}\) | –    | 925                  | –                    | –                    | 925                  | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    |
| v10              | B1u  | 853                  | 861 w                | –                    | 858                  | 860                  | –                    | –                    | –                    | –                    | 859                  | 862                  | –                    |
| \(\gamma 10\)   | –    | 835                  | 830 w                | –                    | 835                  | 825                  | –                    | –                    | –                    | –                    | 832                  | 837                  | 841                  |
| v47              | Eu   | 770 sh               | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    | –                    |
tation wavelength of 406.7 nm); b, from [35] with additions from [32] (excitation wavelength of 406.7 nm); c, from [28] (excitation wavelength of 457.9 nm); d, from [31] (excitation wavelength of 413.1 nm); e, from [31] (excitation wavelength of 413.1 nm); f, from [31] (excitation wavelength of 457.9 nm); g, from [29] (excitation wavelength of 660 nm); h, from [23] (excitation wavelength of 454.5 nm); i, from [35], strong (excitation wavelength of 496.5 nm); j, from [35], observed or very strong in the spectrum (excitation wavelength of 568.2 nm); k, from [35], strong (excitation wavelength of 406.7 nm); l, from [35], strong (excitation wavelength of 514.5 nm); m, medium; s, strong; sh, sharp, w, weak; vw, very weak.

Table 2. Comparison of SERS peak positions

| No | Ab | MPO | AbMPO immunocomplex | Ab + MPO | No | Ab | MPO | AbMPO immunocomplex | Ab + MPO |
|----|----|-----|---------------------|----------|----|----|-----|---------------------|----------|
| 1  | 615 | 615 | 615                 | 28       | 1109 | 1135 |
| 2  | 628 | 649 | 649                 | 30       | 1146 | 1162 |
| 3  | 663 | 664 | 664                 | 31       | 1169 | 1185 |
| 4  | 684 | 710 | 710                 | 32       | 1178 | 1195 |
| 5  | 738 | 741 | 741                 | 33       | 1221 | 1239 |
| 6  | 776 | 779 | 779                 | 34       | 1238 | 1255 |
| 7  | 812 | 814 | 814                 | 35       | 1251 | 1268 |
| 8  | 824 | 826 | 826                 | 36       | 1276 | 1293 |
| 9  | 835 | 835 | 835                 | 37       | 1285 | 1302 |
| 10 | 853 | 853 | 853                 | 38       | 1324 | 1341 |
| 11 | 871 | 871 | 871                 | 39       | 1405 | 1422 |
| 12 | 880 | 880 | 880                 | 40       | 1444 | 1461 |
| 13 | 882 | 882 | 882                 | 41       | 1483 | 1500 |
| 14 | 899 | 899 | 899                 | 42       | 1497 | 1514 |
| 15 | 925 | 925 | 925                 | 43       | 1498 | 1515 |
| 16 | 933 | 933 | 933                 | 44       | 1489 | 1500 |
| 17 | 949 | 949 | 949                 | 45       | 1500 | 1500 |
| 18 | 969 | 969 | 969                 | 46       | 1509 | 1509 |
| 19 | 984 | 984 | 984                 | 47       | 1530 | 1530 |
| 20 | 993 | 993 | 993                 | 48       | 1543 | 1543 |
| 21 | 1007| 1007| 1007                | 49       | 1572 | 1572 |
| 22 | 1012| 1012| 1012                | 50       | 1574 | 1574 |
| 23 | 1013| 1013| 1013                | 51       | 1583 | 1583 |
| 24 | 1023| 1023| 1023                | 52       | 1608 | 1608 |
| 25 | 1064| 1064| 1064                | 53       | 1690 | 1690 |
| 26 | 1074| 1074| 1074                | 54       |       |       |
| 27 | 1079| 1079| 1079                | 55       |       |       |
used different excitation wavelengths (ranging from 406.7 nm to 660 nm) [23,28-31]. Therefore the results obtained suggest that the key identifying MPO peaks are independent of the excitation wavelength, or the Raman method (RRS, CARS or SERS) that was used to collect the data. It is encouraging to also see that the SERS spectrum of the pAb has characteristic peaks similar to previously obtained Raman signals of an IgG. This is not surprising given the structural similarities of the antibodies. The complete list of peaks from Fig. 2 is presented in Table 2.

Figure 2 compares the SERS spectra of MPO, pAb, and the immunocomplex of MPO bound to pAb and Table 2 lists and compares the peaks of each spectrum. Beginning at 500 cm\(^{-1}\) and working towards 1650 cm\(^{-1}\) we observe distinct peak shifts, altered intensities, and unique peaks when comparing MPO, pAb, and their immunocomplex. Signal intensity alone may not be sufficient to differentiate between bimolecular especially in the SERS mode (amplification factors and specific binding may alter the signal intensity significantly) [33]. It may rather be a combination of signal intensity and peak position that can provide a more reliable means for identifying a given sample. The differences shown in Fig. 2 suggest that the immunocomplex formation could result in changes in conformation, orientation of bonds, and changes in the functional groups within the plasmon resonance distance of the gold nanoparticle. New peaks at 871 cm\(^{-1}\), 1109 cm\(^{-1}\), and 1465 cm\(^{-1}\) present in the immunocomplex and not found in either MPO or pAb alone, indicate a tryptophan moiety made now visible in the SERS spectrum, possibly a result of conformational changes after binding. Furthermore, new peaks at 969 cm\(^{-1}\), 984 cm\(^{-1}\), 1146 cm\(^{-1}\) and 1500 cm\(^{-1}\) which are not found in the MPO or pAb signal, indicate the immunocomplex formation. In the Tyr and Amide III region, a peak shift in the pAb spectra from 1276 cm\(^{-1}\) to 1266 cm\(^{-1}\) in the immunocomplex may also correspond to conformational changes.

The critical element in claiming that SERS is capable of identifying binding between MPO and the pAb is the significant difference between a composite spectrum obtained by addition of MPO and pAb and the SERS of the immunocomplex. For the purpose of comparison we are including the spectra of the immunocomplex and the composite spectrum (i.e. sum of pAb and MPO) as normalized average (see Fig. 3). Figure 3 compares the composite and immunocomplex spectra, and for ease of visualization the spectra was divided into 3 sections and presented as Fig. 3a, b, and c. The ability to differentiate such subtle differences without extensive data analysis procedures demonstrates the simplicity of the approach and the sensitivity of the SERS method in differentiating the binding interactions of an immunocomplex from unbound antigen/antibody pair. Relative standard errors (RSE) calculated (n=80) at peak positions that are unique for the immunocomplex are shown in Table 3. RSE at the new peak positions varied significantly, with a minimum deviation (18%) at 1465 cm\(^{-1}\). We attribute these variations to possible orientation differences of the Au particles. It is well established that the amplification factor of the SERS substrate largely depends on the crystal facets to which the molecules are absorbed. Recently Yu et al employed SERS for studying the effect of charge on the orientation of cytochrome c [34] and concluded that the molecules have random orientation on a bare Au nanohole surface. In the present study, it is highly probable that orientation and the crystal facet of the Au particles were totally random. Since the SERS data was collected over a large surface area compared to the size of a cluster of particles it would be important to identify the influence of the crystal orientation on the obtained SERS data, especially on the new peaks. We believe it is possible to minimize these variations by improving the homogeneity of the SERS substrate using the methods proposed by Liu et al [27].

Table 3. Relative standard error at peak positions identified as unique to immunocomplex.

| Peak Position (cm\(^{-1}\)) | Relative Standard Error (%) |
|---------------------------|-----------------------------|
| 870.679                   | 48.0                        |
| 968.762                   | 48.0                        |
| 1109.126                  | 62.0                        |
| 1145.536                  | 51.0                        |
| 1464.528                  | 18.0                        |
| 1500.479                  | 30.0                        |

**CONCLUSIONS**

Our results demonstrate that binding between an antigen (MPO) and its antibody gives rise to unique peaks absent in the composite spectra, derived by mere addition of the respective MPO and MPO-Ab Raman signatures. A valid question is how universal these peaks are and if one should expect to find identical or similar peaks upon binding of any antigen to its antibody. Data on the Raman of IgG antibodies have demonstrated that all IgG Raman spectra are very similar, while antigen Raman spectra depend on their particular structures. For classes of antigen / IgG antibodies where the binding interactions resemble the MPO/MPO-Ab binding, one would expect to find

DOI: 10.5101/nml.v2i2.p74-82

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similar peaks, possibly shifted but in the vicinity of the peaks we have identified. However, for binding pairs where the interaction sites are different chemical entities, totally different peaks would arise. A systematic study of such classes of antigen/Ab pairs would be very useful to create a library of practical significance to many scientific studies.

In summary, we investigated the potential application of SERS in differentiating the bound immunocomplex of an antigen and its antibody from the unbound complex and its components using myeloperoxidase as the model antigen. Obtained results indicate that the SERS spectrum of the immunocomplex is different from that of its parent antigen or antibody, and it is possible to identify conformational changes due to immunocomplex formation. Furthermore, the smallest RSE (18%, n=80) at 1465 cm\(^{-1}\) in the SERS spectra of the immunocomplex supports the notion that further investigation at this particular vibrational mode could provide valuable information towards application of SERS in understanding the changes that occur at a molecular level during binding interactions in biomolecules.

The authors wish to express their gratitude for the expert advice and training provided by Dr. Zhorro Nikolov, Director of the Centralized Research Facilities at Drexel University. This work was partially supported by the W. M. Keck Institute for Attofluidics at Drexel University.

Received 5 March 2010; accepted 30 March 2010; published online 27 April 2010.

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Effects of source-drain underlaps on the performance of silicon nanowire on insulator transistors

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The effects of source-drain underlaps on the performance of a top gate silicon nanowire on insulator transistor are studied using a three dimensional (3D) self-consistent Poisson-Schrodinger quantum simulation. Voltage-controlled tunnel barrier is the device transport physics. The off current, the on/off current ratio, and the inverse subthreshold slope are improved while the on current is degraded with underlap. The physics behind this behavior is the modulation of a tunnel barrier with underlap. The underlap primarily affects the tunneling component of drain current. About 50% contribution to the gate capacitance comes from the fringing electric fields emanating from the gate metal to the source and drain. The gate capacitance reduces with underlap, which should reduce the intrinsic switching delay and increase the intrinsic cut-off frequency. However, both the on current and the transconductance reduce with underlap, and the consequence is the increase of delay and the reduction of cut-off frequency.

Keywords: Silicon nanowire; Insulator transistors; Source-drain

Citation: Sishir Bhowmick and Khairul Alam, “Effects of source-drain underlaps on the performance of silicon nanowire on insulator transistors”, Nano-Micro Lett. 2, 83-88 (2010). doi: 10.5101/nml.v2i2.p83-88

Scaling the transistor sizes has made significant improvement in the cost effectiveness and performance of integrated circuit over the last few decades. The bulk CMOS technology is rapidly approaching the scaling limit and alternate materials or device structures are essential for future electronics. One dimensional nanostructures such as the carbon nanotubes and silicon nanowires are the attractive materials for future nanoelectronics because their electronic properties can be controlled in a predictable manner. Controlled growth of silicon nanowires down to 3 nm diameter [1], their applications as field-effect transistors (FETs) [2-5], logic gates [6] and sensors [7] have been demonstrated.

When the transistors are scaled to nanometer regime, the device performance degrades mainly due to the short channel effects. The scaling of bulk silicon MOSFETs has been facilitated by introducing the device structures with source-drain underlaps [8]. However, large underlaps are required for optimal performance of bulk MOSFETs [9]. The ultra-thin body or FinFETs with undoped channels and bias dependent effective channel lengths have been proposed for optimal device performance [10,11]. Source-drain underlaps have been used to improve the device performance for carbon nanotube transistors [12,13] and silicon nanowire field-effect transistors (SiNWFETs) [14]. Shin uses multiple gates SiNWFETs and studies the subthreshold behaviors with source-drain underlaps [14].

In this paper, we study the effects of source-drain underlaps on device performance, namely the off current, the on current, the inverse subthreshold slope, $S$, the gate capacitance, $C_g$, the intrinsic switching delay, $\tau_i$, and the intrinsic cut-off frequency, $f_T$, of a top gate silicon nanowire on insulator transistor by self-consistently solving the Poisson's and Schrodinger's equations. The off current, the on/off current ratio, and the inverse subthreshold slope are improved while the on current is degraded with source-drain underlaps. The physics behind this behavior is
the modulation of a tunnel barrier by the source-drain underlap. The source-drain underlaps reduce the gate capacitance that should improve the switching performance of the device. However, the transconductance and the on current degrade with underlap and the consequence is the reduction of intrinsic cut-off frequency and increase of switching delay.

**DEVICE STRUCTURE**

Details of the device shown in Fig. 1 are as follows. The silicon nanowire is placed on a thick oxide layer $t_{ox-sub}$. The gate oxide $t_{ox}$ is grown on the nanowire. A gate metal of length $L_g$ is deposited on gate oxide and the exposed regions on both sides of the gate metal are covered by oxide $t_{ox-cs}$. The nanowire under the gate region and the underlaps $L_b$ between the gate and the n-type doped source and drain extension $L_{ex}$ are undoped. The gate length $L_g$ is 10 nm and the gate oxide thickness $t_{ox}$ is 1 nm. The silicon nanowire used in our study has a square cross-section of $5 \times 5 \text{nm}^2$. The substrate oxide, the gate oxide, and the extended oxide are SiO$_2$ with a dielectric constant value of 3.9. The source Fermi level is set to zero (0) and the drain Fermi level to $-qV_{DS}$. The gate metal is assumed to have the same work function value as the nanowire has. The $L_{ex}$ value of 20 nm, the $t_{ox-sub}$ value of 5 nm, and the $t_{ox-cs}$ value of 5 nm are used for Poisson solver so that the fringing electric fields are treated correctly.

![FIG. 1. The cross-sectional view and coordinates of the silicon nanowire on insulator transistor used in this study. Here gate length $L_g = 10$ nm and $L_{ex} = 20$ nm. For Poisson solver, $t_{ox-cs} = t_{ox-sub} = 5$ nm.](image)

**SIMULATION MODEL**

The simulation model uses a self-consistent solution between 3D Poisson’s equation and effective mass Schrödinger’s equation. The 3D Poisson’s equation in cartesian coordinates is

$$
\frac{\partial}{\partial x} \left( \varepsilon \frac{\partial V}{\partial x} \right) + \frac{\partial}{\partial y} \left( \varepsilon \frac{\partial V}{\partial y} \right) + \frac{\partial}{\partial z} \left( \varepsilon \frac{\partial V}{\partial z} \right) = -\frac{\rho}{\varepsilon_0},
$$

where $\varepsilon_0$ is the free space permittivity, $\varepsilon$ is the relative dielectric constant, $V$ is the 3D potential, and $\rho$ is the charge density, which is non-zero in silicon nanowire only. Poisson kernel is created by discretizing Eq. (1) using finite difference. The normal component of electric field is set to zero at the source and drain ends and at the exposed surface of dielectric. Potential is fixed at the gate metal.

The Schrödinger’s equation in 3D cartesian coordinates is

$$
\frac{\hbar^2}{2} \left[ \frac{\partial}{\partial x} \left( \frac{1}{m_x} \frac{\partial \psi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{1}{m_y} \frac{\partial \psi}{\partial y} \right) + \frac{\partial}{\partial z} \left( \frac{1}{m_z} \frac{\partial \psi}{\partial z} \right) \right] + U \psi = E \psi
$$

where $\psi$ is the wave function, $m_x$, $m_y$, and $m_z$ are the effective masses in device coordinates, and $\hbar$ is the reduced Planck’s constant. The nanowire is grown in $<100>$ direction, which is device $x$ coordinate in our study. Ballistic transport is assumed and recursive Green’s function algorithm (RGFA) [15] is used to solve Schrödinger’s equation for charge density and current calculations. The open boundary condition in transport direction $x$ is included in Schrodinger’s equation via self-energy matrices and hard-wall boundary condition is used in the transverse directions ($y$ and $z$). For RGFA, the layer (cross-section) Hamiltonian and layer-to-layer coupling matrices are created by discretizing Eq. (2) using finite difference. With layer Hamiltonian $H_i$ and layer-to-layer coupling matrix $t$, we create the right-connected Green function at each layer (cross-section) from

$$
g_{i,i} = \left( EI - H_i - U_i - t_{i,i}, g_{i,i}, t_{i,i} \right)^{-1},
$$

where $U_i$ is the potential energy at the $i^{th}$ cross-section (layer) obtained from Poisson solver and $I$ is the identity matrix. We discretize Schrödinger’s equation with equal grid spacing, and therefore, $H_i$ is same at each cross-section and $t_{i,i+1} = t$ and $t_{i+1,i} = t^\dagger$. The full Green’s function at the first layer is calculated from

$$
G_{i,i} = \left( EI - H_i - U_i - \Sigma_i - t_i, g_{i,i}, t_{i,i} \right)^{-1},
$$

where $\Sigma_i$ is the self-energy matrix and $g_{0,0}$ is the surface Green’s function. The surface Green’s function is calculated from the decimation method and Ref. [16] has a detailed discussion. The rest $\{2, \ldots, N_i\}$ block diagonal elements of the full Green’s function are calculated from

$$
g_{i,i} = g_{i,i} + g_{i,i}, t_{i,i}, G_{i,i}, t_{i,i}, g_{i,i}.
$$

We calculate the first column blocks of full Green’s function from

$$
G_{j,i} = g_{j,i}, t_{j,i}, G_{j,i}, t_{j,i}, g_{j,i}.
$$

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and the left connected spectral function from
\[ A_i' = G_i^0 \Gamma_{i\delta} G_i^s, \]
where \( \Gamma_{i\delta} = -\text{Im} (\Sigma_i^0 - \Sigma_i^s) \) is the broadening function. The
charge density at each cross-section is calculated from
\[ \rho_{i\delta} = (2q) \frac{dE}{2\pi} \text{diag} \left\{ f_i(E) - f_o(E) \right\}, \]
where \( q \) is the electronic charge, \( f_i \) and \( f_o \) are the source and drain Fermi functions, respectively, and the full spectral function is obtained from \( A_i' = -\text{Im}(G_i^0 - G_i^s) \). The factor 2 at the beginning of right hand side of Eq. (8) includes spin degeneracy. Note that the charge density \( \rho_{i\delta} \) is a column vector of length \( N_s \times N_l \) and is created by taking the diagonal elements of the matrix in the brace of the right hand side of Eq. (8).

The self-consistent loop is started with an initial guess of the potential profile. To generate the initial band profile, we calculate the conduction band position, \( E_{\text{CS}} \), relative to the source Fermi level from charge neutrality. The band profile under the gate region is raised by \( E_g/2 \) (the channel is intrinsic) and that in the drain region is lowered by \( qV_{\text{DS}} \). In other word, the initial profile is a step profile with \( E_{\text{CS}} \) in the source region, \( E_{\text{CS}} + E_g/2 \) under the gate region, and \( E_{\text{CS}} - qV_{\text{DS}} \) in the drain region. Anderson mixing [17] scheme is used for convergence acceleration. Once the convergence is achieved, the coherent drain current is calculated from
\[ I_o = \frac{2q}{h} \left\{ \text{DET}(E) \left[ f_i(E) - f_o(E) \right] \right\}, \]
where transmission coefficient \( T(E) \) is calculated from [15]
\[ T(E) = \text{Tr} \left\{ \Gamma_{i\delta} \left[ A_i' - G_i^s \Gamma_{i\delta} G_i^s \right] \right\}. \]
The calculation is performed for each valley, and the charge density and drain current are obtained by taking sum over the valleys.

**SIMULATION RESULTS**

The silicon nanowire on insulator device used in our simulation is shown in Fig. 1. The channel consists of an undoped silicon nanowire of square cross-section of \( 5 \times 5 \text{ nm}^2 \). A 20 nm doped source-drain extension (\( L_{\text{ex}} \)) with a doping concentration value of \( 2 \times 10^{19} \text{ cm}^{-3} \) is assumed in our simulation. The nanowire is modeled using bulk effective mass parabolic band structure. Using the tight binding (TB) dispersion relation and the bulk effective mass model, Wang et al. [18] argued, using a semiclassical over the top of the barrier model, that the bulk effective mass model overestimates the threshold voltage for wire width < 3 nm and the on current for wire width < 5 nm. Using sp'd's' orbital basis, Zheng et al. [19] show that the bulk masses are quite similar to the confinement masses for wire thickness greater than 3 nm. Shin [14,20] has used bulk effective masses to model silicon nanowire transistors of different gate structures. Poisson solver uses an extension of dielectric \( \varepsilon_{\text{ex}} = 5 \text{ nm} \) in the \( z \)-direction and equal the width of the nanowire on either side of the wire (\( y \)-direction) so that the fringing electric fields emanating from the gate metal are captured. In Fig. 1, the underlap can be varied in two ways: (a) by changing the nanowire length while the gate length is fixed and (b) by changing the gate length while the nanowire length is fixed. We follow method (a) to study the underlap effects on device performance. This is because the underlap as well as the gate length is changed in method (b), and it would be difficult to interpret whether the effect is due to underlap or due to gate length.

The simulated current-voltage characteristics for six different values of overlap are shown in Fig. 2.

![Fig. 2](http://www.nmletters.org)

**FIG. 2.** The simulated current-voltage characteristics for six different values of source-drain underlap. The drain bias is fixed to 0.5 V.

The off current as well as the on current reduces with the increase of underlap. In our study, the off-state current is defined as the drain current at \( V_{\text{GS}} = 0 \text{ V} \) and the on-state current is defined as the drain current at \( V_{\text{GS}} = 0.7 \text{ V} \). Our choice of on-state voltage of 0.7 V comes from the fact that, with the gate metal work function value equal to the nanowire, a flat band situation between the source Fermi level and the channel potential is obtained when the applied gate bias is about half of the band gap, which is 0.7 eV in our study. For a change of \( L_{\text{ex}} \) from 0 to 13 nm, the off current reduces from \( 2.5 \times 10^{-3} \mu\text{A} \) to \( 3.0 \times 10^{-4} \mu\text{A} \) and the on current reduces from \( 22.6 \mu\text{A} \) to \( 2.95 \mu\text{A} \). While the on current reduces by less than one order of magnitude, the off current reduces by almost three orders of magnitude.

To understand the physics of current reduction with underlap, we plot, in Fig. 3, the band profiles superimposed on...
FIG. 3. Conduction band and valence band profiles superimposed on the energy distribution of current for two different values of underlap, 0 nm and 5 nm, at (a) $V_{GS} = 0$ V and (b) $V_{GS} = 0.5$ V. The source Fermi level is at 0 eV and the drain Fermi level is at -0.5 eV.

The energy distribution of current for two different values of underlap, 0 nm and 5 nm, at two different gate biases 0 and 0.5 V.

The source Fermi level is set to 0 eV and the drain Fermi level to -0.5 eV. The current has thermal and tunneling components, and we can calculate them respectively from the energy spectrum of current $J(E) = 2q/\hbar|f(E)|f_s(E) - f_D(E)$ (current per unit energy). The thermal component of drain current can be calculated by integrating $J(E)$ from the conduction band to $\infty$. The tunneling current can be obtained by integrating $J(E)$ from -$\infty$ to the top of the conduction band. At $V_{GS} = 0$ and $L_u = 0$ nm, the tunneling component of current is $2.4 \times 10^{-5}$ μA and the thermal component is $6.5 \times 10^{-7}$ μA. These values are $3.4 \times 10^{-7}$ μA and $3.3 \times 10^{-9}$ μA, respectively, for $L_u = 5$ nm. At $V_{GS} = 0.5$ V, the tunneling and thermal components are $2.99$ μA and $0.83$ μA, respectively for $L_u = 0$ and $0.36$ μA and $0.15$ μA, respectively for $L_u = 5$ nm. The potential barrier width as well as the height becomes larger with the increase of underlap. This reduces both the tunneling and the thermal components of current. The underlap primarily affects the tunneling current, and therefore, the underlap effect is more pronounced in the off-state.

The off current, the on current, the on/off current ratio, and the inverse subthreshold slope are plotted in Fig. 4 as a function of source-drain underlap $L_u$.

Both the on current and the inverse subthreshold slope reduce rapidly with $L_u$ and then get almost saturated when $L_u$ is about 6 nm. The off current and the on/off current ratio, on the other hand, do not show this behavior. If an underlap value of 5 nm is assumed as an optimal design (as the on current and the $S$ do not change significantly after $L_u = 5$ nm), then the inverse subthreshold slope improves from 81 to 73.5 mV/dec, the off current improves from $2.5 \times 10^{-5}$ μA to $3.7 \times 10^{-7}$ μA, the on/off current ratio improves from $9.2 \times 10^5$ to $1.7 \times 10^7$, and the on current degrades from $22.6$ μA to $7.83$ μA when the underlap changes from 0 to the optimal value. The improvement of off-state current and inverse subthreshold slope with gate underlap, and degradation of on-state current with gate underlap for gate-all-around and tri-gate silicon nanowire transistors have been reported by Shin [14]. The off-state current in both types of gate structure improves by four orders of magnitude or higher when the underlap is changed from 0 to 5 nm. The inverse subthreshold slope in their [14] gate-all-around transistors is $\approx 135$ mV/dec at no underlap. This value improves to below 100 mV/dec at an underlap of 5 nm.

Note that the on/off current ratio of $9.2 \times 10^5$ and the off-state current of $2.5 \times 10^{-5}$ μA without source-drain underlap are already decent values and the role of underlap in improving device performance may not be pronounced. To highlight the role of underlap, we simulate the devices with 5 nm gate length and two underlap values 0 and 5 nm. The current-voltage characteristics are shown in Fig. 5.

For these devices, the on/off current ratio is $6.2 \times 10^5$ without underlap and $2.2 \times 10^8$ with 5 nm underlap. The off-state currents are $8.1 \times 10^{-2}$ μA and $7.0 \times 10^{-3}$ μA, respectively for 0 and 5 nm.
underlaps. A 10 nm gate length introduces sufficient tunnel barrier to reduce the tunneling leakage current without underlap and we get a decent value of on/off current ratio. However, the 5 nm gate length device has significantly high off-state current due to narrower tunnel length and the role of underlap is evident in improving device performance, especially the subthreshold performance.

Next we study the effects of source-drain underlaps on the gate capacitance, the intrinsic switching delay, and the intrinsic cut-off frequency. For this, the gate capacitance is calculated from

$$C_s = \int \int dx dy \frac{\delta D}{\delta V_x} + \int \int dy dz \frac{\delta D}{\delta V_y}, \quad (11)$$

where, the first integral takes care of the electric fluxes emanating from the bottom surface of the gate metal and the second integral takes care of the fringing fields emanating from the two sides of the gate metal facing to the source and drain. The intrinsic switching delay is calculated from $\tau_S = C_s V_{DD}/I_{on}$ and the intrinsic cut-off frequency from $f_T = g_m/2\pi C_g$. The transconductance is calculated from $g_m = \partial I_D/\partial V_{GS}$.

The gate capacitance values and the percentage contribution of its different components versus gate bias are shown in Fig. 6. Here $C_b$ is corresponding to the contribution from the fluxes emanating from the bottom surface of the gate metal and is evaluated by the first integral of Eq. (11), and $C_s$ and $C_d$ are the fringing field contributions emanating from the left side of the gate metal to the source, and from the right side of the gate metal to the drain, respectively, and are evaluated from the second integral of Eq. (11). The major contribution comes from $C_b$ and its value ranges from 45% to 51%. The rest, which is almost 50% of the contribution of gate capacitance comes from the fringing fields.

In Fig. 7, we plot the gate capacitance and its different components ($C_b$, $C_s$, and $C_d$), the transconductance, the switching delay, and the intrinsic cut-off frequency as a function of underlap. The gate capacitance reduces with underlap that should reduce the switching delay. However, the on current also reduces with underlap, and the combined effect is increase of the switching delay. The reduction of $g_m$ with underlap should increase $f_T$ and the reduction of $C_g$ with underlap should increase $f_T$. However, the reduction rate of $g_m$ is higher and the consequence is the reduction of $f_T$. The gate capacitance, the

![Image](http://www.nmletters.org)
transconductance, and the cut-off frequency all have significant change with underlap up to 5 nm. After $L_u = 5$ nm, their changes are not large. However, the switching delay does not show this behavior. For a change of $L_u$ from 0 to 5 nm, the $\tau_s$ increases from 0.286 to 1.557 pico second and the $f_T$ reduces from 2.85 to 0.71 THz.

CONCLUSION

A three dimensional quantum simulation is performed for silicon nanowire on insulator transistors to study the effects of source-drain underlaps on device performance and to understand the physics of the effects. The underlap primarily affects the tunneling current and improves the short channel effects of the transistor at the cost of on current and the intrinsic switching performance. Appropriate choice of device structure combined with the source-drain underlaps can improve the device performance that can facilitate the optimal device design.

Received 21 March 2010; accepted 21 April 2010; published online 27 April February 2010.

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Rigid polyurethane foam reinforced with cellulose whiskers: Synthesis and characterization

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A novel nanocomposite of rigid polyurethane foam was prepared by the polymerization of a sucrose-based polyol, a glycerol-based polyol and polymeric methylene diphenyl diisocyanate in the presence of cellulose whiskers. The cell morphology of the resulting foams was examined by scanning electron microscopy which showed both the pure foam and the nanocomposite foam had homogeneous cell dispersion and uniform cell size of approximately 200 μm. Analysis of the foams by Fourier transform infrared (FT-IR) spectroscopy indicated that both samples exhibited signals attributed to the polyurethane including the NH stretching and bending vibrations at 3320 cm⁻¹ and 1530 cm⁻¹, the OC=O vibration at 1730 cm⁻¹ and the CO-NH vibration at 1600 cm⁻¹. FT-IR analysis of the nanocomposite indicated that cellulose whiskers were crosslinked with the polyurethane matrix as the signal intensity of the OH stretch at 3500 cm⁻¹ was significantly reduced in comparison to the spectral data acquired for a control sample prepared from the pure polyurethane foam mixed with cellulose whiskers. According to ASTM standard testing procedures, the tensile modulus, tensile strength and yield strength of the nanocomposite foam were found to be improved by 36.8%, 13.8% and 15.2%, and the compressive modulus and strength were enhanced by 179.9% and 143.4%, respectively. Dynamic mechanical analysis results testified the improvements of mechanical properties and showed a better thermal stability of the nanocomposite foam.

Keywords: Nanocomposites; Cellulose whiskers; Tensile; Compressive; Thermal

Citation: Yang Li, Hongfeng Ren and Arthur J. Ragauskas, “Rigid polyurethane foam reinforced with cellulose whiskers: Synthesis and characterization”, Nano-Micro Lett. 2, 89-94 (2010). doi: 10.5101/nml.v2i2.p89-94

Cellulose is one of the most abundant renewable materials in nature, representing about 1.5×10¹² tons of the total annual biomass production, and is considered a valuable bioresource for addressing society’s increasing demand for environmentally friendly and biocompatible products [1]. It is composed of assemblies of microfibrils where the polymeric chains of β-(1,4)-D-glucose molecules are stabilized by inter- and intra-molecular hydrogen bonding. Upon acid hydrolysis, transverse cleavage happens primarily along the amorphous region of microfibrils, and under certain conditions release cellulose whiskers. These nanocellulose structures typically have a diameter on the order of 10-20 nm and a length of 100-300 nm when prepared from wood pulp or 1100-2000 nm long when derived from tunicates [2]. Cellulose whiskers exhibit a high bending strength of 10 GPa and elastic modulus of 143 GPa [3,4], and changes in electrical, optical, and magnetic properties with respect to the typical micron sized cellulose fibers [5]. There has been a growing interest in cellulose whisker-based composites with both natural and synthetic polymers as the matrix, in part, because of the improvements in the mechanical and thermal properties of the resulting nanocomposites [3,6-10].

Polyurethane (PU) is an important commercial polymer possessing a wide range of physical and chemical properties based on different combinations of starting materials [11]. Rigid PU foams are highly crosslinked polymers with a closed cell
structure which are typically made from polymeric methylene diphenyl diisocyanate and polyols with hydroxyl index ($I_{OH}$) between 300 and 800 and viscosity below 300 Pa·s [12,13]. Rigid PU foams offer low density, thermal conductivity, and moisture permeability properties along with high strength to weight ratio performance attributes. These properties have made PU one of the most common polymeric foam used on a global basis [14], which is reflected in its multitude of applications including ship-building, automotive, furniture, footwear, and packaging [15]. However, for such applications, rigid PU foams still present some disadvantages, such as low thermal stability and low mechanical strength [16]. Therefore, a substantial effort has been directed towards developing high performance rigid PU foams. Glycerol and cellulose fiber modified water-blown soy polyol-based PU foams were reported to have increased density and rigidity [17,18]. Rigid PU foams reinforced with spherical TiO$_2$, platelet nanoclay, rod-shaped carbon nanofibers [19], and pristine and organically-modified layered silicates [14,20] have been investigated and shown to provide a significant enhancement of thermal and mechanical properties. However, to date, little work has been done on developing rigid PU foam reinforced with cellulose whiskers.

In the present study, we summarized the benefits of preparing a rigid PU foam reinforced with 0.75 wt% cellulose whiskers especially with respect to improvements in the mechanical properties of the resulting foam. Scanning electron microscope was used to characterize the cell structure of both foams. FT-IR spectroscopy was performed to study the chemical structure of these materials. Tensile and compressive properties as well as thermal stability were compared between the control foam and nanocomposite foam.

Material and methods

Materials

A commercial fully bleached softwood kraft pulp was used to prepare cellulose whiskers. Sulfuric acid (98 wt%), neopentane, dimethylformamide (DMF) were purchased from VWR. Polymeric methylene diphenyl diisocyanate (MDI) with an average functionality of 2.7 and NCO content of 31.5% (Rubinate M), sucrose-based polyol with a hydroxyl value of 356 mg KOH/g polyol (Jeffol FX 361), glycerol-based polyol with a hydroxyl value of 246 mg KOH/g polyol (Jeffol FX 31-240), dimethylcyclohexylamine (Jeff cat DMCHA), and 1-methyl-4- (2-dimethylaminoethyl) piperazine (Jeff cat TR-52) were all kindly provided by Huntsman Polyurethanes. Silicone surfactant (DABCO DC 5604) was obtained from Air Products and Chemicals, Inc. All chemicals were used as received.

Preparation of Cellulose Whiskers

Cellulose whiskers were prepared following a published method utilizing sulfuric acid [21]. In brief, softwood kraft pulp was ground in a Wiley mill to pass through a 20-mesh screen. Sulfuric acid (64 wt%) and pulp in a ratio of 10 ml/g was reacted at 45°C for 45 min with strong mechanical stirring. The reaction was then halted by adding 10-fold of deionized (DI) water. The sediment was centrifuged for 10 min at 12000 rpm and the precipitate was collected, re-dispersed, and re-centrifuged twice. The product was dialyzed against DI water for 3 days using the regenerated cellulose dialysis tubing with a 12000~14000 molecular weight cut off until the pH of the solution reached 7. Sonication was performed to the neutral whiskers solution for 30 min while sitting in an ice bath. The colloidal suspension was centrifuged for 5 min at 5000 rpm and the cloudy supernatant whiskers were collected and kept at 5°C prior to use.

Preparation of the Pure Polyurethane Foam and Nanocomposite Foam

A rigid PU foam was prepared following a one-shot method [22]. This procedure involved mixing certain amount of polyols (Jeffol FX 31-240 and Jeffol SD-361), neopentane, catalysts (Jeff cat DMCHA and Jeff cat TR-52), and surfactant (DABCO DC 5604) at 600 rpm for 1 min as summarized in Table 1. Polymeric MDI was then added with stirring at 1500 rpm for 20 s. After reacting for 3 min, sufficient polymerization and crosslinking had occurred to solidify the foam. For preparation of the nanocomposite foam, freeze dried cellulose whiskers (0.75 wt% of the total weight of polyols and Polymeric MDI) were first dispersed in DMF by sonication [6], and then polyols were added and mixed followed by removing DMF under reduced pressure. This mixture was employed in an analogous as described for the preparation of the control rigid PU foam. Both foams were cured at room temperature for 48 h before use [23].

Characterizations

The cell structures of the control and nanocomposite foam were examined under a field emission scanning electron microscope (LEO 1530 SEM). Samples were coated with gold palladium using EMS 350 sputter coating. SEM images were obtained using a 5 kV accelerating voltage. FT-IR spectra of

DOI:10.5101/nml.v22.p89-94
both foams were recorded between 4,000 and 600 cm\(^{-1}\) with a resolution of 4.00 cm\(^{-1}\) and 64 scans on a Magna 550 FT-IR spectrometer. Samples were prepared with KBr powder to obtain pellets with a 1 mm thickness.

**Physical Testing**

Tensile tests were performed on the Instron Corporation tensile testing machine 5566 according to ASTM D 638-08 using type IV specimen with dimension: thickness = 4 mm, width = 6 mm, gage length = 25 mm. The crosshead speed was 5 mm/min. Compression tests were carried out with a 17-71 TMI Monitor/ Compression tester according to ASTM C365M-05 on cylindrical specimens with dimension: diameter = 30 mm, height = 15 mm. The crosshead speed was 6 mm/min. For each tensile and compressive data point, five specimens were tested, and the average value (ave.) was taken along with the standard deviation (S.D.).

**Thermal Mechanical Analysis**

Dynamic mechanical analysis (DMA) was carried out with a Q800 TA Instrument in tension clamps to determine the thermo mechanical response of the foams. The specimen was a rectangular strip with dimensions of 10x6x5 mm\(^3\). Measurements were performed at 1 Hz frequency. A temperature scan mode was used from room temperature up to 180°C with a heating rate of 2°C/min. The main relaxation temperatures associated with \(T_g\) were determined from the temperature position of the maximum in tan \(\delta\).

**Results and Discussion**

Two sensitive and important factors to make rigid PU nanocomposite foams are the presence of water and the dispersion of cellulose whiskers in the polymer matrix. As water can act as a chemical blowing agent due to the released carbon dioxide when reacting with isocyanates, its content in cellulose whiskers needs to be controlled. Hence, for this study cellulose whiskers were acquired by freeze drying. We chose neopentane as a physical blowing agent because of its general availability and reported benefits to the physical properties of the resulting foam [24]. Preliminary explorations demonstrated that using a well mixed suspension of cellulose whiskers in DMF resulted in improved dispersion of the whiskers in the polymer matrix. Based on the formulation described in Table 1, the reaction of polyols and polymeric MDI yielded the control foam with a density of 537.5\(\pm\)5.1 kg/m\(^3\). Repeating the same experiment in the presence of 0.75 wt% cellulose whiskers provided a nanocomposite PU foam with a density of 535.9\(\pm\)3.3 g/m\(^3\).

### Table 1. Formulation of the control rigid polyurethane foam.

| Chemicals                                      | wt\% |
|-----------------------------------------------|------|
| Sucrose based polyols                         | 27.90 |
| Glycerol based polyol                         | 16.70 |
| Polymeric MDI                                 | 40.60 |
| Dimethylcyclohexylamine                       | 1.30  |
| 1-methyl-4-(2-dimethylaminopropyl) piperazine  | 0.90  |
| neopentane                                    | 11.20 |
| Silicone surfactant                            | 1.40  |

Scanning electron microscope images of the control foam and nanocomposite foam reinforced with 0.75 wt% cellulose whiskers (see Fig.1) showed that the closed cells had homogeneous dispersion in the PU foams and the cell sizes were approximately 200 µm for both samples. Cellulose whiskers did not alter the closed cell structure presumably because they can act as nucleation sites to promote the formation of fine cell structures [20].

![FIG 1. SEM images of the control foam (a) and the nanocomposite foam (b) (Scale bar: 200µm).](http://www.nmletters.org)

FT-IR spectroscopy was utilized to study the chemical structures of the control and nanocomposite foams (see Fig. 2). The presence of urethane linkages can be readily observed due to the NH stretching and bending vibration absorptions at 3320cm\(^{-1}\) and 1530 cm\(^{-1}\), OC=O vibration at 1730 cm\(^{-1}\), and CO-NH vibration at 1600 cm\(^{-1}\). Methyl group at 2930 cm\(^{-1}\), O-CO at 1230 cm\(^{-1}\), and C-O at 1090 cm\(^{-1}\) are from the polyether polyol and a small contribution of cellulose whiskers.

DOI:10.5101/nml.v2i2.p89-94

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[3]. In order to investigate the interactions between the cellulose whiskers and the PU matrix with the nanocomposite, a spectrum of the control foam which was mechanically mixed with 0.75 wt% cellulose whiskers was recorded. Compared to the mixture of pure PU and cellulose whiskers, the nanocomposite foam shows a reduction in the intensity of the signal centered at 3500 cm\(^{-1}\) which is due to the cellulose O-H stretching vibration and N-H stretching vibration. The decreased signal intensity at 3500 cm\(^{-1}\) for the nanocomposite when normalized to the peak of the carbonyl group at 1730 cm\(^{-1}\) was attributed to the crosslinking of cellulose hydroxyl groups with isocyanate units during polyurethane synthesis.

Tensile stress-strain curves of the control PU foam and nanocomposite foam are shown in Fig. 3. The tensile properties are given in terms of tensile modulus, yield strength and tensile strength as summarized in Table 2. Polyurethane foam reinforced with 0.75 wt% cellulose whiskers has the same density as the control foam; however, it exhibited an increase in tensile modulus, yield strength and tensile strength by 36.8%, 15.2% and 13.8%, respectively.

Compressive stress-strain curves of the control foam and nanocomposite foam are shown in Fig. 4. The compressive properties in terms of compressive modulus and strength are summarized in Table 3. It is observed that with the same density, the modulus and strength of the nanocomposites are dramatically improved by 179.9% and 143.4%, respectively. This substantial improvement in the compressive properties is accomplished at a much lower content of cellulose whiskers than rigid PU foams reinforced with other inorganic nanoparticles up to 5 wt% [19].

There are several factors that can contribute to the mechanical improvements, especially the compressive properties. Cellulose whiskers have an intrinsic high bending strength of 10 GPa, high elastic modulus of 143 GPa and high aspect ratio [3,4,20], and those properties can undoubtedly enhance the mechanical properties of cellulose whisker/rigid polyurethane nanocomposite foam. The high specific surface area of cellulose whiskers may also contribute because of the chemical crosslinking between the cellulose whisker hydroxyl groups and the isocyanate groups. Finally, the improvement of mechanical properties of nanocomposites can also be attributed, in part, to the creation of multiple crack sites and/or branching due to the presence of nanoparticles into the polymer which

![Image](image1.png)

**FIG. 2.** FT-IR spectra of the control foam (a), the nanocomposite foam reinforced with 0.75 wt% cellulose whiskers (b), and a mixture of the control foam and 0.75 wt% cellulose whiskers (c).

![Image](image2.png)

**FIG. 3.** Tensile stress-strain curves of the control foam and the nanocomposite foam.

![Image](image3.png)

**FIG. 4.** Compressive stress-strain curves of the control foam and the nanocomposite foam.

| Whisker (wt%) | Tensile modulus (MPa) | Yield strength (MPa) | Tensile strength (MPa) |
|--------------|-----------------------|----------------------|-----------------------|
|              | Ave±S.D. | Gain (%)  | Ave±S.D. | Gain (%)  | Ave±S.D. | Gain (%)  |
| 0            | 4.37±0.41 | -        | 0.316±0.031 | -        | 0.485±0.043 | -        |
| 0.75         | 5.98±0.37 | 36.8     | 0.364±0.025 | 15.2     | 0.552±0.015 | 13.8     |

**Table 2.** Tensile properties of the control foam and the nanocomposite foam.

DOI:10.5101/nm1.v2i2.p89-94
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Delays the fracture processes in nanocomposites [19].

DMA is a thermal analysis technique that measures the properties of materials as they are deformed under periodic stress. Storage modulus, loss modulus and $\tan \delta$ can be directly given by the test while a variety of other fundamental material parameters can be defined from them such as glass transition temperature $T_g$. In Fig. 5 summarizes the typical DMA curves of storage modulus and $\tan \delta$ within a temperature range from 25°C to 180°C. An abrupt diminution of the storage modulus, which relates to the mechanical failure of the material, can be observed. The appearance of a $\tan \delta$ peak which is so-called sample damping is associated with the material transition and is used historically in literature to define $T_g$ [25]. The modulus value of the nanocomposite foam is significantly higher than the control foam at temperatures below $T_g$. These results support the suggestion that the high mechanical strength of cellulose whiskers and the crosslinking introduced by whiskers improves the mechanical properties of the rigid PU nanocomposite foam. It can also be observed that $T_g$ values of the nanocomposite foam is a little higher than the control foam, which means a comparative or better thermal stability is achieved by the reinforcement of polyurethane with cellulose whiskers.

**Conclusions**

In summary, a rigid polyurethane nanocomposite foam reinforced with 0.75 wt% cellulose whiskers was prepared with homogeneous closed cell dispersion and uniform cell size. The improved mechanical properties and thermal stability of the nanocomposite foam provide a new and promising application of cellulose whiskers with an important synthetic polymer. Ongoing studies will further define the benefits of cellulose whiskers with synthetic and natural-based polyurethane foams.

The authors would like to acknowledge the financial support from the PSE Fellowship program at IPST@GT. The authors would also like to thank Rafael E. Camargo in Huntsman Polyurethanes for providing chemicals and advice.

Received 5 April 2010; accepted 6 May 2010; published online 13 May 2010.

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| Whisker (wt%) | Compressive modulus (MPa) | Compressive strength (MPa) |
|---------------|---------------------------|---------------------------|
|               | Ave ± S.D. | Gain (%) | Ave ± S.D. | Gain (%) |
| 0             | 3.29 ± 0.58  | --       | 0.145 ± 0.045 | --       |
| 0.75          | 9.21 ± 0.0004 | 179.9    | 0.353 ± 0.007 | 143.4    |

Table 3. Compressive properties of the control foam and the nanocomposite foam.
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Fabrication of multi-level 3-dimension microstructures by phase inversion process

Y. Song*

One process based on phase inversion of fillers in microstructures for the fabrication of multi-level three-dimensional (3-D) microstructures is described using SU-8, a kind of epoxy photoresist, as the model constructing materials. This process is depicted by use of the routine photolithography technique to construct the top layer of 3-D microstructures on the bottom layer of 3-D microstructures layer by layer. This process makes it possible to fabricate multi-level 3-D microstructures with connectors at desired locations, and to seal long span microstructures (e.g. very shallow channels with depth less than 50 μm and width more than 300 μm) without blockage. In addition, this process can provide a sealing layer by the solidification of a liquid polymer layer, which can be as strong as the bulk constructing materials for microstructures due to a complete contact and cross-linking between the sealing layer and the patterned layers. The hydrodynamic testing indicates that this kind of sealing and interconnection can endure a static pressure of more than 10 MPa overnight and a hydrodynamic pressure drop of about 5.3 MPa for more than 8 hours by pumping the tetrahydrofuran solution through a 60 μm wide micro-channels.

Keywords: Microstructures; Multi-level; Fabrication; Photolithography; Phase inversion; Sealing

Citation: Y. Song, “Fabrication of multi-level 3-dimension microstructures by phase inversion process”, Nano-Micro Lett. 2, 95-100 (2010). doi: 10.5101/nml.v2i2.p95-100

Micro and nano fluidic devices are useful not only because they allow manipulation with fast response times, handle small fluid volumes, sense and control flows and pattern substrates on small lengths scale, but also promise selectively address the cellular cell [1,2]. As a result of the uniform reactor conditions in mass and heat transfer similar as in microbial cells obtained, a high degree of reaction control is observed [3,4]. Modern developments in the design and utilization of micro fluidic devices for fluid transport have found many applications, ranging from the life science industries for pharmaceuticals and biomedicine (drug discovery, drug delivery and detection, diagnostic devices) [4,5] to industrial applications of combinatorial synthesis (such as, stereoselective synthesis [3], nanoparticle synthesis [6-8], rapid in-situ chemical analyses and high throughput screening [9,10]). Hence, there is an urgent need for developing rapid and economically viable prototyping processes for manufacturing micro fluidic devices with suitable materials compatible with the application environment [11,12].

In order to realize lab-on-a-chip in practical sense, micro-temperature controller (heat-exchanger and T-sensor), micro pressure controller, micro flow rate controller, micro separator, micro detector and other micro devices are necessarily integrated in one chip, most probably realized in multi-level 3-D microstructures with connectors at any locations. Building microstructures in 3-D still presents significant challenges when working with the inherently planar geometries that are accessible through projection photolithography [11-15]. Alternatives to photolithography for fabrication schemes that “write” patterns serially in metals and polymers either carve in a wise manner from a solid object or cause localized deposition of material in a series manner [15,16]. However, these methods are often limited in the connectivity and dimensionalities of structures they can
generate. The idea by transferring 2-D patterns to 3-D microstructures through pseudo-3-D patterns in a cylindrically symmetrical substrate remains a challenge to form multi-level 3-D microstructures with connectors and lose the convenience to build complicated microstructures with more than one layer of 3-D structures on the normal chip [16].

Compared with silicon, glass or stainless steel based micro fluidic devices, polymer based micro devices are more promising as microchips because of the availability of different types of polymers, low cost and ease of fabrication using LIGA, embossing, casting, injection molding and imprinting process [17,18]. Careful selection of polymers and fabrication process can lead to commercially viable fabrication processes and different application environment for micro fluidic devices [12]. SU-8, an epoxy-based negative photo resist, has been gaining much attention as a material of choice for the fabrication of microstructures and microchannels due to its superior chemical and mechanical properties besides its ease of fabrication using photolithography process [12,16,18-20]. However, when using SU-8 for the fabrication of multi-level 3-D microstructures, there are still some issues that need to be addressed. The multi-level 3-D microstructures fabricated with connectors at desired locations, a strong binding interface for complete sealing of these microstructures and the sealing for long span microchannels with a shallow depth (<50 μm) without any blockage are still not trivial problems although many processes have been developed for these problems [11,12,16]. The developed process by thermal binding two pre-patterned solid SU-8 layers to form multi-level 3-D microstructures needs to overcome the micro gas-gaps between the two solid layers or operate under vacuum and then to form a complete inter-connecting between the two layers, which is usually not a trivial matter [11,12,21]. Furthermore, it is difficult to get connecting parts at some desired locations between the two layers or needs tedious alignment [11,21]. In addition, once the substrate is used to support the SU-8 layer, additional work is required to release the substrate from the SU-8 layer for the construction of other levels. Otherwise, it will lose the opportunity to construct additional SU-8 layer on the pre-formed SU-8 layers [11].

This report demonstrates a flexible process based on the phase inversion of fillers in the pre-patterned microstructures for the design, the fabrication and the sealing of multi-level 3-D microstructures. This process favors to get free-selected connectors between two contacting layers and the strong sealing of the long span microstructures with depth less than 50 μm using the routine photolithography process.

Figure 1 shows the schematic diagram for the fabrication of multi-level 3-D microstructures with freely designed connectors. The first layer with embedded structures is formed according to our previous process (see Fig. 1(i)) [12]. Then a kind of filler (i.e. wax, polymers, etc.) will be heated above its melting point and filled into the pre-formed microstructures (see Fig. 1(ii)) by a syringe at a large opening orifice. The second layer of liquid photo resist (e.g. SU-8) is coated on the filled first level of microstructures (see Fig. 1(iii)) after the liquid filler changes to solid. Using the routine photolithography process described in reference 12, the second level of microstructures can be constructed in the second layer of photo resist on the first level of microstructures (see Fig. 1(iv)). The second level of microstructures is then filled again by the fillers like step 2 (see Fig. 1(v)). Then the third layer of the liquid photo resist (e.g. SU-8) will be spin-coated on the top of the filled 2 levels of microstructures (see Fig. 1(vi)). Similar as previous steps, the third layer can be constructed and refilled by the fillers (see Fig. 1(vii)). If necessary, hundreds of levels of microstructures can be fabricated layer by layer (see Fig. 1(viii)) just following the previous steps (ii-iv). When all the desired microstructures with necessary levels are constructed, the whole microstructures can be further sealed according to their applications by constructing the last layer of photo resist using the routine photolithography process (see Fig. 1, ix-x). After all the constructions are completed, the whole multi-level 3-D microstructures can be increased to a certain temperature (above the melting points of fillers) to liquefy the fillers. Then the liquid fillers can be pushed out of the whole microstructured chip by compressed air flow. If necessary, the sealed or opened microstructures can be washed by a certain solvent to dissolve the fillers on the walls of microstructures to make sure the multi-level 3-D microstructures are clean.

Since the top level can be constructed as the routine photolithography without any trouble on the patterned bottom microstructures, the sealing location and opening locations on the bottom level of microstructures can be designed and formed in the top level of microstructures much flexibly. In addition, since the top layer is constructed from the liquid photo resist, the top layer and the bottom layer can be completely contacted to avoid the micro gas-gap from the coarse surface, leading to intensive crosslinking reaction between the two contacting layers using the standard photolithography procedure.
Clearly, the key issue in this process is to find suitable fillers that can reversibly change their phases, from liquid to solid before constructing the top layer, and then from solid to liquid after finishing all construction, either by adjusting operating temperature or by solvents. In addition, there are three basic requirements for this kind of fillers. Firstly, this kind of fillers should have enough low viscosities in liquid phase. Secondly, the melting temperature of the fillers used should be compatible to the common photolithography process of photo resists (e.g. SU-8) [12], or the melting temperature should be around or above the pre-baking and post-baking temperature of the photo resist, and the fillers should not be dissolved into the developer for the photo resist. For SU-8, the melting temperature range of these fillers can be about 70~200°C according the SU-8 photolithography process and the thermal stability of SU-8 [12]. Thirdly, the fillers can be dissolved by water or some kind of solvent that will not dissolve the cured photo resists. A kind of high melting temperature wax, such as mondang wax (d=1.09g/cm³, Tm = 75~87°C, Guangzhou Yu Feng Chemical Trade Co., Ltd), or Polyethylene (PE) wax (XH-200, Tm = 105~115°C , XH 206, Tm = 135~145°C , Hero Tianjin International Trade Co., Inc.), or Polyvinyl Alcohol (Mw=31000~50000, Tm = 200°C; d=1.267 g/cm³, Aldrich), etc., will be very suitable for these purposes. These waxes can be dissolved by tetrahydrofuran or acetone and the PVA can be dissolved in hot water. While the crosslinking SU-8 photo resists have enough resist to these solvents. Thus, the fillers in liquid phase under a suitable temperature can flow into the microstructures (i.e. channels, mixtures, orifices, chambers) by forming a liquid surface a little bit below the wall of microstructures to prevent from overflowing to other parts when the next layer of liquid SU-8 is coating on. After they change to solid by reducing the temperature, a uniform solid surface together with the patterned structures is formed, which acts as a supporting substrate for the liquid photo resist. Since this process is suitable for liquid coating, the interfaces which may be filled by air bubbles between two layers using other solid thermal bonding process (i.e. hot embossing) can be avoided, particularly for large areas of uneven surfaces. Thereby, a complete contact

FIG. 1. Schematic diagram for the fabrication of multi-level 3-D microstructures by the phase inversion process: (i) Construct the first layer of micro structures with embedded structures on the substrates by the routine UV-LIGA process; (ii) Fill the filler into the 1st layer micro structures; (iii) Spin coating the 2nd SU-8 layer for the 2nd level microstructure; (iv) Construct the 2nd level SU-8 microstructure by the routine UV-LIGA process; (v) Fill the filler into the 2 level micro structures; (vi) Spin coating the 3rd SU-8 layer for the 3rd level microstructure; (vii) Fabricate the 3rd level SU-8 micro structure by routine UV-LIGA process and fill the filler in to the 3rd level micro structures; (viii) Fabricate several level microstructures by repeating (ii)-(iv) to form desired levels of microstructures; (ix) Spin coating the last SU-8 layer for sealing; (x) Seal the multi-level microstructures by solidification of the SU-8 layer after exposure under UV-light.
between layers can be obtained that will result in a strong binding.

Using this phase inversion process, many complex multi-layer 3-D microstructures can be constructed although some of them cannot be built up using multi-layer fabrication process mentioned by some reports [11,21]. In the following, some typical multi-level 3-D microstructures will be demonstrated using SU-8 as constructing materials and mondang wax or PE wax as fillers.

Figure 2 shows the typical complex 2-level 3-D microchannels with flexible connectors using the phase inversion process. In Fig. 2(a), the transparent optical photograph clearly indicates the first layer channels is covered by the second layer channels, which can have lots of opened connecting parts in the first layer channels to the second layer channels for exchanging information, which may be used as mixers for two-layer liquid-liquid mixing or liquid-gas mixing. Their cross-section optical image (see Fig. 2(b)) suggests that the bottom surface of the second layer channels is connected with the top surface of the first layer channels with many connecting parts. Figure 2(b) shows that the sealing surface is uniformly flat without any blockage and deformation, which can be further evidenced by their Scanning Electron Microscope (SEM) images for some local places (see Fig. 2(c) and 2(d)). Figure 2(c) clearly shows that the 80 μm wide channels in the top level are opened and connected with the 80 μm depth channels in the bottom level at the arrowed locations. Figure 2(d) shows the cross-section images of one bottom 400 μm wide channel and one top 80 μm wide channel, where the top surface (i) of the bottom channel has the same height as the bottom surface (ii) of the top channel along the dashed line, indicating the depth of the bottom channel about 80 μm.

Figure 3 shows SEM images for other two typical 2 level 3-D microstructures with channels connected with large orifices or chambers. Figure 3(a) is one large chamber (diameter of 2000 μm) with doped bottom U-shaped channel (80 μm) inside, suggesting no trace blockage in the channels and the very smooth bottom surface of the chamber. This kind of design may be used for further fabrication of some functional materials inside the channels as sensing units. When the sensing function is finished, the microfluid in the chamber can leave the chamber by directly entering the bottom U-shape channels. Figure 3(b) and 3(c) are the reversed design of Fig. 3(a) with two top channels (80 μm) passing through the large chamber (diameter of 1800 μm). Since there are some interface effect between the wax and the wall of the preformed chamber and some volume change of wax during the pre-baking and post-baking of the top layer of SU-8 photo resist, the edge parts in the chamber are not as uniform as those

![FIG 2. Connected two-layer 3-dimensional microchannels. (a) The flat optical image of one cross-connected two-layered 3-D microchannels; (b) The optical images of the cross-section for the connected two-layer 3-D microchannels; (c) The SEM image on the cross-section and two channels at the 2nd layer; (d) The SEM image with two-layered one channel at the bottom layer and one channel at the top layer.](http://www.nmletters.org)
in Fig. 3(a) and show some convex edge-bird effects. But the opening between the chamber and the two channels are very perfect, as shown by the optical microscope image (see Fig. 3(c)).

In the microfabrication, another important field is to sealing very shallow channels with long span, which is also difficult since the blockage occurs often. Using the developed phase inversion process, it will become easy for channels with depth of less than 50 μm and span more than 300 μm. Figure 4 shows the optical image (a) and the SEM image (b) of the cross-section of one channel with 40 μm depth and 350 μm width, which has sharp surrounding rims and abrupt sidewall-to-bottom transitions without any significant blockage.

FIG. 3. Typical examples of microstructures with connecting parts. (a) The SEM image of one big reservoir with one U-shape channels in the bottom; (b) The SEM image of one big reservoir connecting with two top channels; (c) The optical image of the big reservoir connecting with two top channels clearly showing the opening parts of the two channels on the top of the reservoir.

FIG. 4. One typical sealed shallow microchannel with height of 40 μm and width of 350 μm. (a) The optical image of one shallow microchannel; (b) The SEM image of the cross-section of this shallow microchannel (dashed square in (a)).

Unlike other solid bonding process (e.g. hot-embossing), the interlayer for the sealing between the two layers cannot be envisioned since a uniform and complete contact interface is formed during sealing process using the liquid photo resist (e.g. SU-8) (see Fig. 2, Fig. 3 and Fig. 4), which will lead to ultra-strong bonding between two contacting layers. In order to investigate the bonding strength, samples of the multi-level microchannels with width of 60 μm, depth of 400 μm and length of 25 cm are sealed by a layer of 400 μm thick SU-8 and post-backed at 150°C for 30 min, and then tested by pumping the tetrahydrofuran solution through the micro-channels at a flow rate of ~15.0 ml/min and a frequency of 2 Hz for more than 8 hours, corresponding to a calculated dynamic pressure drop across the channels about 5.3 MPa. The result suggests that no tracing leakage was observed. The sealed microfluidic channels (with width of 60 μm and a sealed layer of 400 μm thick) were also tested under the static air pressure, indicating that these two layers cannot be debonded even at a pressure of 10 MPa overnight. When the sealed layer was reduced to 60 μm thick, the SU-8 film without bonding with the sub-layer is broken while the SU-8 film bonding with the sub-layer is still united together. These results indicate that the sealing process preserves the potential to reach the binding as strong as the bulk photoresist (i.e. SU-8 100) [22].

In summary, one process based on the phase inversion of fillers inside the preformed 3-D microstructures has been successfully developed for multi-level 3-D microstructure construction using SU-8 as model constructing materials. This process makes it possible to seal channels with depth no more than 40 μm, and to construct desired multi-level 3-D microstructures with connectors at necessary locations flexibly.
with interlayer bonding as robust as the bulk constructing materials (e.g. SU-8).

This work is financially supported by the National Science Foundation of China (No. 50971010), New Teacher Foundation of Beihang University (211109), New Teacher Funds of Education Ministry of China (2008-00061025) and SRF and SEM funds of Education Ministry of China.

Received 31 March 2010; accepted 5 May 2010; published online 18 May 2010.

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Synthesis, characterizations and hydrophobicity of micro/nano scaled heptadecafluorononanoic acid decorated copper nanoparticle

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Copper nanoparticle was synthesized in the presence of heptadecafluorononanoic acid by the conventional solution immersion method at room temperature from the copper plate, as a resource material. The bulk etching rate was calculated by the weight loss method. The pale green colored Cu-HDFN was characterized by Fourier transform infrared spectroscopy, UV-Visible spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and contact angle measurements and the results are critically analyzed.

Keywords: Copper nanoparticle; Etching; Hydrophobicity

Citation: Hung-Hsia Chen, R. Anbarasan, Long-Sheng Kuo, Meng-Yu Tsai, Ping-Hei Chen and Kuei-Feng Chiang, “Synthesis, characterizations and hydrophobicity of micro/nano scaled heptadecafluorononanoic acid decorated copper nanoparticle”, Nano-Micro Lett. 2, 101-105 (2010). doi: 10.5101/nml.v2i2.p101-105

Synthesis of nanosized material from the bulk resource material is a fascinating field of research because of its novelty and application in various science and engineering fields. Various techniques are employed for the generation of nanosized material from its bulk one [1-10]. Generally, thermal treatments are employed for this purpose, unfortunately it requires costly instruments. In order to outwit this problem our research team has followed a conventional chemical method. The advantages of the present investigations are 1) economically cheaper, 2) no use of expensive and hazardous chemicals and hence it is a pollution free method, 3) the resultant material has hydrophobic characters and 4) the simultaneous coating of hydrophobic material on the surface of the bulk resource material. A modified copper surface with super hydrophobic characteristics could be used either in vapor chamber or heat pipe that has been widely employed for heat spreading of electric devices.

Recently, Song et al [11] reported about the electroless replacement deposition method for the generation of super hydrophobic copper substrate. Super hydrophobic surfaces based on copper hydroxide nano needles were reported by Wu and co-workers [12]. Wang and his research team [13] studied the super hydrophobic copper films. The super hydrophobic character was supported by water contact angle measurement reports. Super hydrophobic Cu(OH)₂ nano tubes from copper foil were reported in the literature [14]. Other authors also reported about the super hydrophobic copper plate surface by different techniques [15-17]. Fluoro compounds exhibit hydrophobic character with water surface and this urged us to do the surface modification of copper plate by heptadecafluorononanoic acid (HDFNA). By thorough literature survey, we could not find any report based on the synthesis of Cu nano particle in the presence of HDFNA. In the present investigation we took this job as a challenge and
successfully synthesized the Cu nano particle in the presence of HDFNA with simultaneous coating on the same in ethanol medium at room temperature for the first time, with Fourier transform infrared (FTIR) spectroscopy, UV-Visible spectroscopy (UV-vis), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and contact angle measurement reports. When compared with the literature reports, the present investigation yielded an economically cheaper method to produce the nanosized copper from the resource material with hydrophobic character. Moreover, this investigation didn’t use any hazardous or toxic solvents to produce nanosized copper and hence is an eco-friendly method.

**Experiment**

**Materials**

HDFNA (Fluka, USA) and ethanol (Sigma Aldrich, USA) were purchased and used as received. A copper plate with the purity of 99.99% was used as a resource material for the generation of copper nano particle. The dimensions of the copper plate are mentioned below: weight of copper plate-4.1310 g, length-6 cm, breadth-2 cm, area-12 cm².

**Surface treatment and etching rate of the copper plate**

The copper plate with the above mentioned dimensions was rubbed with metal paper and ultrasonicated for 1 h to remove the metal oxide from the surface. 50 mL of double distilled water (DD) was used to wash the surface of the copper plate. 0.10 g (0.02 M) of HDFNA was dissolved in 100 mL of ethanol in a 150 mL beaker under mild stirring condition in the open air atmosphere. Accurately weighed and dried copper plate was immersed in the reaction medium with mild stirring under the influence of atmospheric air, which activated the chemical etching process. After 12 hours of etching, the copper plate was removed from the reaction medium and dried at 80°C for 1 h in an air oven. The dried copper plate was weighed accurately and change in mass was tabulated. Meanwhile, 2 mL of the aliquot was taken from the reaction medium and the UV-Visible absorbance was measured. Both the weight and absorbance measurements were carried out in a regular period of time to measure the etching rate. The bulk etching rate \( V_B \) was calculated from the following equation.

\[
V_B = \frac{\Delta m}{2Ap \Delta t}
\]

Where \( \Delta m \) is the mass difference, \( A \) is the etched surface area, \( p \) is the density of the copper plate and \( t \) is the etching time. At the end of the etching reaction, the etched copper plate was removed from the beaker and the content of the beaker was diluted with water and frozen below 0°C in the refrigerator. Thus frozen contents were dried under vacuum by using a freeze drier. After 48 hours of freeze drying, the pale green mass obtained was HDFNA coated copper nano particle and the product was subjected to analytical characterizations. 3 mg of the Cu-HDFN sample was made disk with 200 mg of spectral grade KBr and the FTIR spectrum was measured between 400 and 4000 cm⁻¹ with the help of Perkin Elmer Spectrum 100 series instrument. Jasco V-570 instrument was used for UV-Visible spectrum measurement. Surface morphology of the sample was measured by JSM 6300, Jeol product, SEM instrument. The size of the copper nano particle was determined by TEM 3010, a product of JEOL. The binding energy of HDFNA decorated copper nano particle was determined by XPS (XPS, Thermo Scientific, Theta Probe, UK). The contact angle of Cu-HDFN coated copper plate was determined by VCA 2500, Taiwan instrument.

**Experimental results and discussion**

**FTIR study**

Figure 1a shows the FTIR spectrum of Cu-HDFN. A peak at 546 cm⁻¹ confirmed the presence of F in Cu-HDFN. A twin peak at 656 cm⁻¹ indicated the Cu-O stretching vibration. The metal salt (Cu-O-C) peak is appeared at 1144 cm⁻¹. The metal salt carbonyl group is appeared at 1689 cm⁻¹. Generally the ester carbonyl group will appear at 1725 cm⁻¹. In the present investigation, the ester carbonyl peak was red shifted due to the smaller size and highly electron withdrawing nature of F atom.

![FIG. 1. FTIR spectrum of HDFNA decorated copper nano particle.](http://www.nmletters.org)
in the HDFNA backbone. The C-H symmetric and anti-symmetric stretching is observed at 2856 and 2932 cm\(^{-1}\) respectively. A twin peak around 3400 cm\(^{-1}\) declared the presence of Cu co-planarity. An ionic interaction is existing between the copper nanoparticle and HDFNA. Thus the FTIR spectrum confirmed the various functionalities presented in the HDFNA coated copper nano particle. For the sake of comparison, the FTIR spectrum of pure HDFNA is shown in Fig. 1 as 1b. The important peaks are characterized below: A peak at 3752 cm\(^{-1}\) indicates the presence of intermolecular hydrogen bonding due to the carboxyl group of HDFNA. A broad peak around 3500 cm\(^{-1}\) is responsible for the carboxyl OH stretching. Generally, the long chain carboxylic acid will not exhibit the C-H stretching around 2900 cm\(^{-1}\) in its acidic form. The carbonyl peak is observed as a doublet around 1725 cm\(^{-1}\) due to the free and hydrogen bonded carboxyl group. By comparing Fig. 1a and b, appearance of Cu co-planarity, C-H stretching, sharp C=O stretching, C-O-Cu and Cu-O stretching confirmed the formation of Cu-HDFN.

**UV-Visible spectroscopy**

Figure 2 indicates the UV-Visible spectrum of Cu-HDFN. A negative absorbance peak was observed at 322 nm. This peak is quite natural and due to the n to Pi* transition [18] of the HDFNA decorated copper nano particle [19]. The hindered transition can be explained on the basis of highly negatively charged HDFNA decorated co-planarized copper nano particle. It is important to note that the absorbance value increases with the increase of etching time. After 24 hours of etching, the absorbance value drastically increased and thereafter it linearly increased. This explained the molecular oxygen influenced chemical etching process. After 24 hours of etching, the diffused copper reacted with the HDFNA in the presence of atmospheric air to produce the Cu-HDFN and the same was coated on the copper plate. As a result of Cu-HDFN coating on the copper plate, the free surface available for the chemical etching is restricted and a slow increase in the chemical etching process is observed. The inset of Fig. 2 confirms the same concept. The plot was made between etching time and absorbance at 322 nm. The plot showed a steep increase in absorbance up to 48 hours and then showed a linear increase with the etching time. This confirmed that up to 48 hours, the chemical etching was the only reaction occurred inside the reaction medium, after 48 hours, etching and coating were the competitive reactions. Hence, after 48 hours the absorbance value was linearly increased with the etching time.

**SEM report**

Figure 3 indicates the surface morphology of Cu-HDFN. Figure 3a represents the plate like morphology. Figure 3b indicates the cauli flower like morphology. Flower like morphology is responsible for superhydrophobicity nature of a material [4]. The SEM results proved that the HDFNA decorated copper plate was slowly converted into super hydrophobic one due to the simultaneous coating of Cu-HDFN on the copper plate. Further, this can be confirmed with the contact angle measurement and will be discussed in the forthcoming sessions.

**TEM analysis**

Figure 4 shows the topography of HDFNA coated copper nano particle. Figure 4a represents the agglomerated form of copper nano particle with the size of 400 nm. Figure 4b represents the sphere topography of copper nano particle with the size of 10~65 nm. Figure 4c indicates the individual nano particle size of 20 nm with the distorted sphere morphology. The distortion is due to the adsorption of HDFNA on the surface of the copper nano particle. The TEM images concluded that during the synthesis of super hydrophobic Cu plate, nanosized copper was diffused into the reaction medium from the copper plate resource material and formed HDFNA coated copper nano particle and the same was coated on the
surface of the resource material. This is an eco-friendly and economically cheaper method to produce the copper nano particle from the resource.

**XPS analysis**

Figure 5 shows the XPS of HDFNA decorated copper nano particle. It showed the binding energy of Cu2p$_{3/2}$ and Cu2p$_{1/2}$ at 933.08 and 950.2 eV [20] respectively. A signal at 933.08 eV confirmed the existence of Cu nano particle (zero oxidation state). Moreover, the % of copper was found to be 1.07%. The F1s level of F in HDFNA decorated copper nano particle was determined at 687.23 eV with 35.92% content. The C1s and O1s peaks of HDFNA are observed at 281.9 and 530.8 eV respectively. The XPS analysis concluded that the HDFNA is coated on the surface of the copper nano particle. Again this supported the core-shell like structure of HDFNA decorated copper nano particle.

**Determination of bulk etching rate**

The bulk etching rate was determined from equation (1). It was interesting to note that while increasing the etching time, the colorless reaction medium turns into pale green. This ultimately indicated that the concentration of the diffused copper nano particle was increased. The etching rate was determined from the plot drawn between the etching time and the difference in mass (see Fig. 6a). The slope value was derived by linear fit method as 0.31 mg/cm$^2$.H. An important point noted here is that the weight loss after 24 hour is drastically increased. At the same time the concentration of copper in the reaction medium was increased and this can be further supported by the UV-Visible absorption value (i.e.) the absorption value increased with the increase of the etching time. In 1995, Bryce et al. reported about the bulk etching rate of copper in ferric chloride solution as 0.27 mg/cm$^2$·s [5]. Our report is in accordance with them. Figure 6b indicates the effect of etching time on the water contact angle, and discussed in the next session.

**Contact angle measurement**

The contact angle measurement confirmed the hydrophobicity nature of the HDFNA coated copper nano particle. After 5 days of etching, the CA was determined as 140.7°. This proved the hydrophobic nature of the Cu-HDFN coated copper plate at the 5th day. Figure 7 shows the picture of CA measured for the Cu-HDFN coated copper plate. Thus the contact angle co-supported the SEM morphology of HDFNA coated copper nano particle. While increasing the etching time, the water contact angle of copper plate was increased due to the chemical etching reaction. Figure 6b represents the effect of etching time on the water contact angle. Due to the surface etching reaction, the water contact angle was increased.
Conclusions

The important points are presented here as conclusions. 1) The HDFNA decorated copper nano particle was successfully synthesized with the C.A of 140.7°. The formation of Cu-HDFN was confirmed by FTIR spectroscopy by noting a peak at 656 cm⁻¹. 2) Further, the presence of copper in Cu-HDFN was confirmed by UV-Vis spectroscopy at an absorbance value of 322 nm. 3) The absorbance value increased with the increase of etching time. 4) The bulk etching rate was determined as 0.31 mg/cm².H. 5) XPS analysis confirmed the binding energy of Cu₂p₃/₂ at 933.08 eV. SEM (cauli flower morphology), C.A measurement (140.7°) and TEM (10~65 nm size) combinedly declared that the HDFNA coated copper nano particle is a suitable candidate for the manufacture of copper nano particle with hydrophobic character. The above points inferred that our methodology yielded an economically cheaper and eco-friendly method with the nanosized copper particle.

Received 29 March 2010; accepted 5 May 2010; published online 20 May 2010.

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Extracellular synthesis of silver nanoparticles using dried leaves of *Pongamia pinnata* (L) pierre

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Extract of oven dried leaves of *Pongamia pinnata* (L) Pierre was used for the synthesis of silver nanoparticles. Stable and crystalline silver nanoparticles were formed by the treatment of aqueous solution of AgNO₃ (1mM) with dried leaf extract of *Pongamia pinnata* (L) Pierre. UV-visible spectroscopy studies were carried out to quantify the formation of silver nanoparticles. Transmission electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy were used to characterize the silver nanoparticles. TEM image divulges that silver nanoparticles are quite polydispersed, the size ranging from 20 nm to 50 nm with an average of 38 nm. Water soluble heterocyclic compounds such as flavones were mainly responsible for the reduction and stabilization of the nanoparticles. Silver nanoparticles were effective against *Escherichia coli* (ATCC 8739), *Staphylococcus aureus* (ATCC 6538p), *Pseudomonas aeruginosa* (ATCC 9027) and *Klebsiella pneumoniae* (clinical isolate). The move towards extracellular synthesis using dried biomass appears to be cost effective, eco-friendly to the conventional methods of nanoparticles synthesis.

Keywords: Extracellular synthesis; Silver nanoparticle; *Pongamia pinnata*; Antibacterial

Citation: Rajesh W. Raut, Niranjan S. Kolekar, Jaya R. Lakkakula, Vijay D. Mendhulkar and Sahebrao B. Kashid, “Extracellular synthesis of silver nanoparticles using dried leaves of pongamia pinnata (L) pierre”, Nano-Micro Lett. 2, 106-113 (2010). doi: 10.5101/nml.v2i2.p106-113

Nanobiotechnology, a branch of Nanoscience has been playing a decisive role in 21st century in deciphering diverse tribulations particularly in the field of farming, medication and electronics. Nanoscience poses a basic scientific challenge as it requires a control over the connections between atoms. All physiochemical methods of nanoparticle synthesis are having inherent limitations up to a certain extent which impose an important hurdle in the maturation of this science. The improvement in the experimental procedures for controlling shape and size of nanoparticles is one of the challenges for material scientists. Equally, the development of ecofriendly cost effective methods is also in demand. Consequently, viable production of metal nanoparticles is mostly studied.

The possibility of utilizing biological materials for metal nanoparticle synthesis has appeared as the most efficient and greener approach [1]. The present decade has witnessed the rapid shift in synthesis strategies from physicochemical methods to biological agents such as bacteria, fungi and plants for nanoparticle synthesis [2-4]. The idea of employing biomaterials for nanoparticle synthesis is an extension of the well established fact that the various organisms such as diatoms, magnetostactic and S-layer bacteria are capable to synthesize nanoscale materials [5].

Both living and dead microorganisms are gaining importance by virtue of their facile assembly of nanoparticles. Prokaryotic bacteria have primarily attracted the attention in the area of biosynthesis of silver nanoparticles [6-8]. However, reduction of silver ions using these microorganisms results in the deposition of the particles in the periplasmic space and hence requires either sonication or use of permeabilizing agents.
to extract the silver nanoparticles [9]. Filamentous fungi on the other hand are capable of synthesizing the silver nanoparticles extracellularly but the downstream processing and the biomass handling make them difficult [10-12].

The biomaterial as reducing agent is a viable alternative to the current physiochemical methods which utilize intense energy, hazardous chemicals and are expensive. Furthermore, metal nanocolloids produced by the physiochemical methods tend to aggregate with time and consequently cannot be stored for longer time. Amongst biomaterials, the phytosynthetic method is a viable alternative to prokaryotes and fungi since the downstream processing and the handling of the biomass is easier. Consequently the phytosynthetic method is preferred. Bioreduction of gold and silver ions to yield metal nanoparticles using *Geranium* leaf broth [13], Neem leaf broth [14], lemongrass extract [15], *Tamarind* leaf extract [16], *Aloe vera* plant extracts [17] and *Gliricidia sepium* (Jacq.) Kunth ex Walp leaf broth [18] has been reported. The above methods have made use of the plant broth prepared by boiling finely chopped fresh leaves and some of them require addition of stabilizing agents or the use of ammonia [17] as accelerating agents. Moreover, the procedure involves continuous agitation of the broth after the addition of the salt solution.

In the present study the leaf broth prepared using dried leaf biomass of *Pongamia pinnata* (Linn) Pierre was used to synthesize silver nanoparticles from silver nitrate (AgNO₃). *Pongamia pinnata* is rich in nitrogenase and secondary metabolites which are medicinally important. Comparative experiments were carried out to explore the effect of biomass dosage on the reduction of the silver ions and uniformity of the synthesized nanoparticles. The efficacy of the synthesized nanoparticle against bacterial strains was also studied.

**Experiments**

**Preparation of dried biomass**

The twigs containing mature leaves of *Pongamia pinnata* (L.) Pierre were collected from University of Mumbai campus. The mature, undamaged and disease free leaves were selected and washed thoroughly with water using Teepol and later the surface was sterilized with 0.1% HgCl₂ for 2-3 minutes under laminar air flow. The washed leaves were kept in the oven at 40°C overnight for drying. The biomass used for the reduction was prepared by grinding the dried leaves followed by sieving the leaf powder using 15 mesh size sieves.

**Synthesis of silver nanoparticles**

In typical synthesis process, accurately weighed dried leaf biomass of *Pongamia* (0.1 g, 0.5 g, and 1 g) was added to the sterile 50 mL 1mM aqueous AgNO₃ [Merck] solution in Dippy’s jar of 250 mL under aseptic conditions. The jars were then incubated at room temperature under static condition.

**UV-Vis Spectrum analysis**

The bioreduction of silver ions was monitored by UV Visible absorption measurements at room temperature as function of time using Shimadzu UV 1700 spectrometer. The reduction of silver ions was confirmed by qualitative testing of supernatant (obtained after centrifugation) with NaCl, no precipitation was observed. 1 mM AgNO₃ solution was used for base line correction.

**X-ray Diffraction (XRD) Measurements**

The completely bioreduced sample was concentrated in concentrator (Eppendorf) at 60°C to reduce the volume of the reaction mixture. The concentrated solution was then centrifuged [Hermle Labortechnik (Siemensstr 25 78564 Wehingen)] at 15000 rpm for 15 minutes. The pellet obtained, was washed and redispersed in deionized water. The repeated centrifugation and redispersion in deionized water was carried out to remove the water soluble biomolecules such as proteins and secondary metabolites. XRD measurements of purified silver nanoparticle solution casted onto the glass substrate was carried out using Phillips PW 1830 instrument operating at a voltage of 40 kV and current of 20 Ma with Cu K(α) radiation of 1.54187 nm wavelength.

**Transmission Electron Microscopy (TEM) Measurements**

The sample purified as stated in XRD measurement section was sonicated (Vibronics VS 80) for 5 minutes. A drop of the sonicated solution was placed on carbon coated copper grid and later exposed to infrared light (30 minutes) for solvent evaporation. TEM measurements were performed on PHILIPS model CM 200 instrument operated at an accelerating voltage of 200 kV with resolution of 0.23 nm.

**Fourier Transform Infrared (FTIR) Spectroscopy Measurements**

The FTIR measurements were carried out for both the dried biomass of *Pongamia pinnata* leaves and washed silver nanoparticle solution, free from any biomass residue or compound except the capping ligand using Perkin Elmer (Spectrum One) spectrophotometer.

**Antibacterial Studies**

The antibacterial activity of silver nanoparticles was studied against *Staphylococcus aureus* (ATCC 6538P), *Escherichia coli* (ATCC 8739), *Pseudomonas aeruginosa*.
(ATCC 9027) and Klebsiella pneumoniae (Clinical isolate) by agar disc diffusion method [19]. The 18 hrs-revived cultures were prepared in nutrient broth [composition (gm/litre): peptone 15.0; yeast extract 3.0; sodium chloride 6.0; D (+) glucose 1.0].

The two replica of the respective microorganism were prepared by spreading 50 µl (inoculum concentration 1.2 × 10^6 CFU/mL) of revived log phase culture on the nutrient agar plate [composition (gm/litre): peptone 15.0; yeast extract 3.0; sodium chloride 6.0; D (+) glucose 1.0; agar-agar 12.0] with the help of spreader. Discs of Whatman filter paper No. 40 was made having diameter of 10 mm. The pure aliquot of plant material of 25 µl was placed on the first disc as a control. 25 µl sample of synthesized silver nanoparticles (prepared using 0.1 gm dried leaves) was placed on the second disc. The third disc was used for 25 µl Ampicillin (Ampilin 250 Hetero healthcare Ltd.) with concentration of 125 µg/mL as standard. The Petri plates were incubated in dark at 37°C.

Results and Discussion

Development of easy, reliable and eco-friendly methods helps in endorsing extra interest in the synthesis and application of nanoparticles which are good for mankind [1]. In this context the utilization of biological systems for nanoparticle synthesis is notable alternative for the advancement of multifaceted approach. Biological systems have shown the ability to interact with metal ions and reduce them to form metallic nanoparticles [20-21].

UV -Visible studies

The relationship between the UV-visible radiation absorbance characteristics and the absorbate’s size and shape is well established [13-18]. Consequently size and shape of nanoparticles in aqueous suspension can be judged by UV-visible absorbance studies. By employing the variable amount of biomass (0.1, 0.5, 1.0 g) with 1.0 mM AgNO_3, the effect of biomass amount on rate of bioreduction and size of the target product was studied. The amount of the biomass was found to play a decisive role in size distribution of Ag nanoparticles. Figure (1) illustrates the absorbance spectra of reaction mixture containing aqueous silver nitrate (1 mM) and Pongamia leaf broth (prepared from 0.1 g dried leaf powder) at various time intervals. The absorption spectra recorded divulge the production of Ag nanoparticles within 9 hrs. Upon addition of the plant broth to the solution of AgNO_3, the solution changed from yellowish green to brown (see Fig. 2 (b)). The final color deepens and turns brownish with the increase of time. The intensity of the absorbance increased as the reaction proceeded. Silver nanoparticles display intense yellowish brown colour in water. This intense colour arises from the surface plasmons, which are dipole oscillation arising when an electromagnetic field in the visible range is coupled to the collective oscillations of conduction electrons [13].

It is well known that the metal nanoparticles in size ranging from 2 to 100 nm exhibit strong but broad surface plasmon peak. Minima at ~320 nm observed in all the reaction mixtures correspond to the wavelength at which the real and imaginary parts of the dielectric function of silver almost vanish [17]. With the increase in the particle size, the optical absorption spectra of metal nanoparticles that are dominated by surface plasmon resonances (SPR) shift towards longer wavelengths. The position of absorption band also strongly depends upon dielectric constant of the medium and surface-adsorbed species [22]. As indicated by Mie's theory, spherical nanoparticles give rise to a single SPR band in the absorption spectra, whereas anisotropic particles confer two or more SPR bands depending on the shape of the particles [23]. In present investigation, all reaction mixtures show a single SPR band revealing spherical shape of silver nanoparticles, which was further confirmed by TEM images.

The reduction of Ag^+ ions occurs rapidly, completing within 9 hrs of reaction. This was confirmed by performing qualitative analysis for the presence of free Ag^+ ions with NaCl in the supernatant obtained after centrifugation of the reaction mixture. The silver nanoparticles obtained from the reaction mixture containing 1mM AgNO_3 and 0.1 g of dried leaf powder were purified and further analyzed. The silver nanoparticles were found to be remarkably stable even after 6 months. Rapid synthesis of stable silver nanoparticles using Geranium leaf broth (20 g of leaf biomass) and 1mM aqueous AgNO_3 have been reported by Sastry et al. [13]. Shivshankar et al. [14]
reported rapid synthesis of stable silver, gold and bi-metallic Ag/Au core shell nanoparticles using 20 g of leaf biomass of *Azadiracta indica* and 1mM aqueous AgNO₃. Similarly, Pratap and coworkers [17] reported synthesis of gold and silver nanoparticles using *Aloe vera* leaf extract with the use of ammonia as an accelerating agent for synthesis of silver. All of them used leaf broth prepared by boiling finely chopped fresh leaves and the procedure involves continuous agitation of the broth after the addition of the salt solution.

The present study reports the use of oven dried leaf biomass, which is free from external stabilizing and accelerating agents and does not require continuous agitation. The reduction of the silver ions is moderately rapid at the ambient conditions. This is novel and intriguing to the material science as the studied leaf biomass has the capability to reduce metal ions at ambient conditions. Furthermore the biomass handling and processing is less stringent since it does not require boiling or subsequent treatment. Instead of sun drying the leaf biomass was oven dried at 40ºC to avoid the possible contamination due to particulate matter. Also the sun drying process is time consuming and has geographical constraints.

**TEM Analysis**

TEM images which constitute large number of uniform nanoparticles revealed that the Ag nanoparticles produced by reduction of Ag⁺ ions with 0.1 g, biomass are predominantly spherical (see Fig. 3(a-c)). At low magnification (see Fig. 3(c)) TEM images show large number of silver nanoparticles which are quite polydisperse and ranges in size from 20~50 nm with calculated average size of 38 nm. Figure 3(b) shows clear morphology of silver nanoparticles. These nanoparticles appear to have assembled into very open, quasi-linear superstructures rather than a dense closely packed assembly [13]. The figure also reveals that nanoparticles are not in physical contact but are evenly separated. The images also clearly show an approximate 5 nm thickness coating around the nanoparticles which can be assigned to bioorganic compounds present in the leaf broth [13]. This is evident by number of sharp Braggs reflection observed in the XRD spectra.

**XRD studies**

The XRD-spectrum of purified sample of silver nanoparticles synthesized using 0.1 g dried leaf biomass and 1mM AgNO₃ (see Fig. (4)) show a number of Braggs reflections that can be indexed on the basis of the face centered cubic structure of silver. The peaks observed in the spectrum at 2θ values of 38.06°, 44.64°, 64.58° and 77.62°, corresponds to 111, 200, 220, and 311 planes for silver, respectively. This clearly indicates that the silver nanoparticles formed by the reduction of Ag⁺ ions by the *Pongamia* leaf extract are crystalline in nature [7]. As mentioned in method section, the silver nanoparticles were repeatedly centrifuged and redispersed in sterile distilled water prior to XRD and TEM analysis, ruling out possibility the presence of any free compound/protein that might independently crystallize and give rise to Braggs reflections. The intense background noise is due to the protein shell around the nanoparticles [24]. An unidentified peak at 46º

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**FIG. 2.** Showing colour changes (a) 1 mM AgNO₃ and (b) synthesized nanoparticles showing brownish colour.

**FIG. 3.** TEM Images of Ag Nanoparticles (a) 2 Lakh magnification; (b) Nanoparticle showing capping; (c) 1 Lakh magnification; (d) Particle size distribution extracted from TEM images (235 particles counted).
FTIR studies

The precise mechanism of the bioreduction is not fully understood. Mukherjee and co-workers [10] have reported that the reduction process of Ag⁺ to Ag nanoparticles occurs possibly in the presence of enzyme NADPH-dependent dehydrogenase. The exact route in which the electrons are shuttled is matter of investigation. Also the information regarding environment responsible for high stability of metal nanoparticles is not comprehensively available. FTIR analysis of isolated silver nanoparticles free from proteins and water soluble compounds was done in this direction. The analysis of IR spectra gives an idea about biomolecules bearing different functionalities which are present in underlying system. Representative spectra (see Fig. (5b)) manifest major IR bands at ~1651, 2083, 3418 cm⁻¹, while the minor bands at ~1079 and ~1538 cm⁻¹. The FTIR spectra of dried biomass (see Fig. (5a)) show bands at ~1069, ~1240, ~1314, ~1390, ~1447, ~1515, ~1561, ~1620, ~1653, ~1734, ~2852, ~2920, ~3306, ~3441 and ~3656 cm⁻¹.

The band around ~1069 cm⁻¹ can be assigned to the ether linkages or C-O- [14,25], whereas, the band around ~1314 cm⁻¹ and 1390 cm⁻¹ can be assigned to geminal methyls [14] (see Fig. (5a)). To a large extent, the band at ~1069 cm⁻¹ might be contributed by the C-O- groups of the polyols such as flavones, terpenoids and the polysaccharides present in the biomass [25]. The absorbance band centered at ~1620 and ~1653 cm⁻¹ (5a) is associated with the stretching vibration of C=C- or aromatic groups [14,25]. The band around ~1734 can be assigned to C=O stretching vibrations of the carbonyl functional group in ketones, aldehydes, and carboxylic acids [13,17,25]. Besides, the spectrum (5a) also exhibits two intense bands at ~2852 and ~2920 cm⁻¹, respectively assigned to the symmetric and asymmetric stretching vibration of sp³ hybridized -CH₃ groups that are not observed in the spectrum (5b) of isolated silver nanoparticles, suggesting that -CH₃ groups are probably absent in solution [10].

The band at ~1651 cm⁻¹ (5b) is due to amide I bond of proteins, indicating predominant surface capping species having -C=O functionality which are mainly responsible for stabilization. However, albeit there is adequate evidence for the presence of surface bound proteins, the conclusion regarding the presence of the specific compound cannot be made unless the individual component is isolated and identified. Furthermore, an interfacial interaction of these biomolecules with core particles is the matter of investigation. Sastry and co-workers [16] have reported that the species having dipole moment such as acetone binds strongly and reversibly to the gold nanoparticles in vapor phase. This supports the strong binding of -C=O functionality from medium, to the core particles. A broad intense band at ~3400 cm⁻¹ in both the spectra can be assigned to the N-H stretching frequency arising from the peptide linkages present in the proteins of the extract [10]. The shoulders around the band can be identified as the overtone of the amide-II band and the stretching frequency of the O-H band, possibly arising from the carbohydrates and/or proteins present in the sample. The flattening of the shoulders in Fig. (5b) indicates decrease in the concentration of the peptide linkages in the solution [10]. The spectra (see Fig. (5b)) also exhibit broad asymmetric band at ~2100 cm⁻¹ that can be assigned to the N-H stretching band in the free amino groups of silver nanoparticles.

The bands of functional groups such as -C-O-C- , -C-O- and -C=O are derived from the heterocyclic water soluble compounds present in the dried biomass, which as seen in the IR spectra of dried biomass is in good agreement with the value reported in the literature. Since these band disappeared in the IR spectra of the final product it can be concluded that the reducing agents are largely derived from these water soluble heterocyclic compounds. Yin et al [26-27] has reported the
presence of prenylated flavonoid derivatives pongaflavanol and tunicatachalcone in *Pongamia pinnata*, where the latter one is proposed as biogenic precursor of the former one and the reaction is effected by flavanone/dihydroflavanol NADPH-dependent reductase. Therefore, it reflects that water soluble heterocyclic compounds such as flavones are the reducing and capping ligands of the nanoparticles.

In the polyl synthesis, gold nanoparticles are extensively studied for, and both oxygen and nitrogen atoms of pyrrolidone unit can facilitate the adsorption of PVP on to the surface of metal nanostructures to fulfill the protection of nanoparticles [28]. Likewise, the oxygen atoms herein might facilitate the adsorption of the heterocyclic components on to the particle surface in stabilizing the nanoparticles. It is also evident from the differences in the peak for dried powder and silver nanoparticles that the flavones are responsible for the bioreduction. Flavones could be adsorbed on the surface of the metal nanoparticles, possibly by interaction through π-electrons of carbonyl groups in the absence of other strong ligating agents in sufficient concentrations [14]. On comparing Fig. (5a) and (5b) it can be outlined that the disappearance of the band around 1069 cm$^{-1}$ shows that the polyols are mainly responsible for the reduction of silver ions.

**Antibacterial Studies**

Antibacterial activity of biogenic silver nanoparticles was evaluated by using standard zone of inhibition (ZOI) microbiology assay. The nanoparticles showed inhibition zone against all the studied bacteria (see Table (1)), (see Fig. (6)). Maximum zone of inhibition was found to be 12 mm for *Staphylococcus aureus* ATCC 6538P and *Klebsiella pneumoniae* (Clinical isolate) and minimum of 8 mm for *E. coli*.

Silver nitrate which is readily soluble in water has been exploited as an antiseptic agent for many decades [29]. Dilute solution of silver nitrate has been used since the 19th century to treat infections and burns [30]. The exact mechanism of the antibacterial effect of silver ions is partially understood. Literature survey reveals that the positive charge on the Ag ion is crucial for its antimicrobial activity. The antibacterial activity is probably derived, through the electrostatic attraction between negative charged cell membrane of microorganism and positive charged nanoparticles [31-33]. However, Sondi and Salopek-Sondi [34] reported that the antimicrobial activity of silver nanoparticles on Gram-negative bacteria was dependent on the concentration of Ag nanoparticles and was closely associated with the formation of pits in the cell wall of bacteria. Accumulation of the Ag nanoparticles in the pits results in the permeability of the cell membrane, causing cell death. Similarly, Amro et al [35] suggested that depletion of the silver metal from the outer membrane may cause progressive release of lipopolysaccharide molecules and membrane proteins. This results in the formation of irregularly shaped pits and hence increases the membrane permeability. Similar mechanism has been reported to be operative by Sondi and Salopek-Sondi [34] in the membrane structure of *E. coli* during treatment with Ag nanoparticles. Recently, Kim and co-workers [36] have reported that the silver nanoparticles generate free radicals that are responsible for damaging the membrane. They also speculated that the free radicals are developed from the surface of the silver nanoparticles. Lee et al [37] investigated the antibacterial effect of nanosized silver colloidal solution against *S. aureus* and *K. pneumoniae* after padding the solution on textile fabrics. Shrivastava et al [38] studied antibacterial activity against *E. coli* (ampicillin resistant), *E. coli*, *S. aureus*, and *S. typhi* (multi-drug resistant). They reported that the effect was dose dependent and was more pronounced against gram-negative organisms than gram-positive ones. They found that the major mechanism through which silver nanoparticles manifest antibacterial properties was either by anchoring or penetrating the bacterial cell wall, and modulating cellular signaling by dephosphorylating putative key peptide substrates on tyrosine residues [38]. Similarly, Chun-Nam and coworkers [39] reported that the silver nanoparticles target the bacterial

| Sr. No. | Name of the Strain               | Diameter of Zone of Inhibition in mm |
|---------|----------------------------------|-------------------------------------|
|         |                                  | Ampicillin | AgNO$_3$ | Silver Nanoparticles |
| 1       | *Pseudomonas aeruginosa* (ATCC 9027) | 15         | 7        | 10                      |
| 2       | *Escherichia coli* (ATCC 8739)   | 20         | 6        | 8                       |
| 3       | *Klebsiella pneumoniae* (Clinical isolate) | 16         | 7        | 12                      |
| 4       | *Staphylococcus aureus* (ATCC 6538P) | 20         | 8        | 12                      |

DOI:10.5101/nml.v2i2.p106-113
membrane, leading to a dissipation of the proton motive force resulting in the collapse of the membrane potential. They also proposed that the silver nanoparticles mediated antibacterial effects in a much more efficient physicochemical manner than Ag\(^+\) ions. The antibacterial efficacy of the biogenic silver nanoparticles reported in the present study may be ascribed to the mechanism described above but it still remains to clarify the exact effect of the nanoparticles on important cellular metabolism like DNA, RNA and protein synthesis.

**Conclusion**

The method represents an example of clean, nontoxic and ecofriendly method for obtaining silver nanoparticles. The capping around each particle furnish uniform chemical environment formed by the bioorganic compound present in the leaf broth, which may be mainly responsible for the stabilization of the particles. This method provides a simple and efficient route for the synthesis of nanoparticles with tunable optical properties directed by particle size. From the point of view of nanotechnology this is a significant advancement to synthesize silver nanoparticles economically.

The silver nanoparticles show distinct polydispersity as it shows particle size between the ranges of 20 to 50 nm with an average size of 38 nm. The maximum nanoparticles showed particle size of 30 nm, distinct cap was observed around the nanoparticles, which is due to the flavonoids present in the leaf broth of Pongamia pinnata and is mainly responsible for the reduction of silver ions. The identification of capping agents and tapping the enzymes responsible for the reduction process may open up new avenues in the field of nanoparticle stabilization.

Investigation on the antibacterial effect of nanosized silver colloidal solution against *S. aureus* (ATCC 6538), *K. pneumoniae*, *P. aeruginosa* (ATCC9 027) and *E. coli* (ATCC 8739) reveals high efficacy of silver nanoparticles as a strong antibacterial agent. This can be useful in food industries, cosmetic industries and medicines. The important question regarding biocompatibility of nanoparticles is yet to be answered.

We sincerely acknowledge the facilities provided by The Institute of Science and Tata Institute of Fundamental Research, Mumbai.

Received 4 March 2010; accepted 30 March 2010; published online 20 May 2010.

DOI:10.5101/nml.v2i2.p106-113

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A low-voltage and energy-efficient full adder cell based on carbon nanotube technology

Keivan Navi*, Rabe'e Sharifi Rad, Mohammad Hossein Moaiyeri and Amir Momeni

Scaling problems and limitations of conventional silicon transistors have led the designers to exploit novel nano-technologies. One of the most promising and feasible nano-technologies is CNT (Carbon Nanotube) based transistors. In this paper, a high-speed and energy-efficient CNFET (Carbon Nanotube Field Effect Transistor) based Full Adder cell is proposed for nanotechnology. This design is simulated in various supply voltages, frequencies and load capacitors using HSPICE circuit simulator. Significant improvement is achieved in terms of speed and PDP (Power-Delay-Product) in comparison with other classical and state-of-the-art CMOS and CNFET-based designs, existing in the literature. The proposed Full Adder can also drive large load capacitance and works properly in low supply voltages.

Keywords: CNFET; Low-Voltage; Full-Adder; Minority-Function; Nanotechnology

Citation: Keivan Navi, Rabe'e Sharifi Rad, Mohammad Hossein Moaiyeri and Amir Momeni, “A low-voltage and energy-efficient full adder cell based on carbon nanotube technology”, Nano-Micro Lett. 2, 114-120 (2010). doi:10.5101/nml.v2i2.p114-120

Scaling down the feature size of MOSFET devices in nanometer, leads to serious challenges, such as short channel effects, very high leakage power consumption and large parametric variations. Due to these limitations researchers become eager to work toward new emerging technologies such as Quantum Automata (QCA) [1], Nanowire transistors [2] and Carbon Nanotube Field Effect Transistors (CNFET) [3]. By the mentioned problems of nanoscale CMOS technology, which makes it unsuitable for low-power and low-voltage applications in the near future, these nano-devices could replace the conventional silicon MOSFET in the time to come. However, due to the similarities between the infrastructure and functionality of the conventional MOSFET devices with CNFETs and also because of the ballistic operation of CNFETs, it could be more promising and achievable, compared to other nano-devices. Recently some efforts have been done for designing circuits based on CNFET such as multiple valued logic circuits [4,5], arithmetic circuits [6] and so on, taking advantages of its unique attributes. However, among these circuits arithmetic circuits could be more interesting, due to their vast range of applications. Many VLSI systems such as microprocessors, DSP architectures and nano-micro systems [7,8,9] have arithmetic unit, which is also included in their critical path. One of the most important and basic arithmetic units is Full Adder, which could be the basic structure of many complex arithmetic systems and as a result its performance directly affects the performance of the whole system. Therefore, it is necessary to design novel Full Adder structures with higher performance and lower power consumption, based on the emerging nano technologies. In this paper a new energy-efficient 1-bit Full Adder cell is proposed, which takes advantage of CNFET devices and high density Carbon Nanotube Capacitors (CNCAP) [10]. The proposed circuit is also compared with the classical and state-of-the-art CMOS and CNFET-based Full Adders, with different styles, which are briefly introduced in this section.
CCOM Full Adder cell [11], which has 28 transistors, is the classical CMOS Full Adder cell designed based on the conventional complementary style of design. CMOS-Bridge Full Adder cell [12], which has 24 transistors, is a state-of-the-art CMOS Full Adder cell designed based on a low-power style of design, called Bridge style. Hybrid1 [13] and Hybrid2 [14] Full Adder cells, which have 26 and 24 transistors, respectively, are composed of different high-performance 2-input XOR-XNOR circuits and hybrid CMOS style. TG Full Adder cell [15], which has 18 transistors, is the classical high-performance Full Adder cell, designed based on Transmission gates (TG). The CNT-FA-1, presented in [4] (see Fig. 1(a)), is minority function based Full Adder with 8 transistors and 7 capacitors. CNT-FA-2 presented in [5] (see Fig. 1(b)), which is composed of 12 transistors and 8 capacitors, is based on majority-not, NAND and NOR functions. A minority function is used to produce \( C_{\text{out}} \) signal. Another minority function is exerted on input capacitors and two NAND and NOR gates to implement \( \text{Sum} \) signal.

Carbon Nanotube Field Effect Transistors (CNFETs)

Carbon Nanotube (CNT), which was discovered in 1991 by S. Iijima is a nano-scale tube created by rolling sheets of graphite [16]. Recently, it has become one of the new research trends in physics, chemistry, mechanics, biology and electronics due to its outstanding properties. A CNT could be single-wall (SWCNT) or multi-wall (MWCNT), due to the number of cylinders used in its structure. A SWCNT could be metallic or semiconducting due to its chiral number \((n_1, n_2)\). Chiral number defines the form of the placement of the carbon atoms along a CNT. If \( n_1 - n_2 = 3k \ (k \in \mathbb{Z}) \), the SWCNT is semiconducting otherwise it is metallic [17]. Electronic device designers exploit semiconducting SWCNT as the channel of the Carbon Nanotube Field Effect Transistor (CNFET), which was first fabricated by Tans, Verschueren, and Dekker in 1998 [18]. CNFETs, like MOSFETs, have P-type and N-type devices. However, the great advantage of CNFET devices is that the P-type and N-type CNFETs with the same device size have the same mobility, which simplifies the process of transistor sizing, specifically in complex circuits with a large number of transistors [19]. Furthermore, CNFET based circuits are faster and have lower average power consumptions, in comparison with current MOSFET-based designs [19].

The current-voltage (I-V) characteristics of the CNFET and MOSFET devices are similar. In addition, similar to the MOSFET devices, CNFETs have threshold voltage, which is required for turning on the device. The threshold voltage of a CNFET is inversely proportional to the diameter of the CNT as it is shown in Eq. (1). This makes it possible for CNFET to be turned on, at the required voltages and therefore, designing complex circuits with better performance becomes more feasible [17].

\[
V_{th} \approx \frac{E_g}{2e} = \frac{\sqrt{3}}{3} \frac{aV_n}{eD_{CNT}} \approx 0.43 \frac{V}{D_{CNT} (nm)}
\]

Where \( E_g \) is the band gap, \( V_n (\approx 3.033 \text{ eV}) \) is the carbon
\( \pi \)-\( \pi \) bond energy in the tight bonding model, parameter \( a \) (= 0.249 nm) is the carbon to carbon atom distance, \( e \) is the unit electron charge, and \( D_{\text{CNT}} \) is the diameter of CNT. \( D_{\text{CNT}} \) itself could be calculated based on the following equation [17]:

\[
D_{\text{CNT}} = a \times \sqrt{n_1^2 + n_2^2 + n_3^2} \approx 0.078 \times \sqrt{n_1^2 + n_2^2 + n_3^2} \quad (2)
\]

Three different types of CNFETs have been already presented in the literature. The first type is Schottky Barrier CNFET (SB-CNFET) (see Fig. 2(a)), which is composed of a metal-semiconducting nanotube-metal junction, and operates under the principle of direct tunneling by way of the Schottky barrier formed by nonideal contact between metal and carbon nanotube. The main drawback of this kind of CNFET is that the metal-nanotube contact actually limits the transconductance of the CNFET in the ON state and decreases the current delivery capability, which is a significant parameter for high speed operation in a device. In addition, strong ambipolar attributes of SB-CNFET limit the usage of this type of device in customary logic families. SB-CNFET is appropriate for medium to high-performance applications. The second type of CNFET is the band-to-band tunneling CNFET (T-CNFET) (see Fig. 2(b)) and has super cut-off characteristics and low ON currents, which makes it very appropriate for ultra-low-power and subthreshold applications but is not suitable for very high-speed applications. The third kind of CNFETs, which can make a compromise between very high-speed operation and low power consumption, is the MOSFET-like CNFET (see Fig. 2(c)). In this type of device, Potassium doped drain and source nanotube regions have been fabricated and field-effect behaviour and unipolar characteristics have been achieved. The main advantage of MOSFET-like CNFET is that its source-channel junction has no Schottky Barrier and as a result, it has significantly high ON current. Therefore, MOSFET-like CNFETs are very suitable for ultra-high-performance digital applications [3].

Based on the mentioned advantages and disadvantages of different types of CNFETs and also due to more similarities between MOSFET-like CNFETs and MOSFETs in terms of working and characteristics, in this paper MOSFET-like CNFETs are utilized for designing the proposed circuit.

**Proposed Full Adder Cell**

The proposed Full Adder design is implemented by means of majority function, based on carbon nanotube technology. This design is based on the idea that the \( C_{\text{out}} \) function is the same as 3-input majority function shown in (3) [4].

\[
C_{\text{out}} = \text{Majority}(A,B,C) = AB + AC + BC 
\quad (3)
\]

This type of majority gate is made of input CNCAPs and a CNFET-based inverter. Figure 3 illustrates a 3-input majority-not gate designed by this method.

\[
\text{Sum} = A \oplus B \oplus C
\]

\[
= ABC + \overline{A} \cdot \overline{B} \cdot \overline{C} + \overline{A} \cdot B \cdot \overline{C} + A \cdot B \cdot \overline{C} = ABC + (AB \cdot AC \cdot BC)(A + B + C)
\]

\[
= ABC + C_{\text{out}} \cdot C_{\text{out}} + C_{\text{out}} \cdot (A + B + C) = ABC + C_{\text{out}} \cdot (AB + AC + BC) + C_{\text{out}} \cdot (A + B + C) = \text{Majority}(A,B,C,C_{\text{out}},C_{\text{out}})
\]

The construction of the proposed design has two stages. \( C_{\text{out}} \) is implemented by means of majority-not function in the first stage and in the second stage a five-input majority-not function is used for implementing \( \overline{\text{Sum}} \). Figure 4 illustrates the proposed design. Figure 4(a) exhibits the basic scheme of the design and the circuit is shown in Fig. 4(b). The majority structure is implemented by three input capacitors. These three input capacitors prepare an input voltage that is applied for driving \( n \)-CNFET. Through superposition of input capacitors, increase in input voltages is scaled at point \( x \). These capacitors are also connected to \( C_{\text{out}} \) with a capacitor. If \( "C_1" \) is the capacitance of each input capacitors, then \( 2 \times C_2 \) is the

![FIG 2. Different types of the CNFET device. (a) SB-CNFET (b) T-CNFET (c) MOSFET-like CNFET.](http://www.nmletters.org)
The next majority-not gate, which is composed of $M_2$ and $M_4$ transistors, has two input capacitors $2 \times C_2$ and $3 \times C_2$. $2 \times C_2$ is driven by $C_{out}$ and the input signals drive $3 \times C_2$. When all of the inputs are “0”, the $C_{out}$ will be “1”. In this case, the 5-input majority-not gate has three low inputs and two high inputs. Therefore, the $\text{Sum}$ signal is “1” and $\text{Sum}$ is “0”. In the case of $\text{Sim}="1"$ (for instance “100” input pattern), the majority-not gate has two inputs in the “0” state and three inputs in the “1” state. Hence the $\text{Sum}$ signal will be high. When $\text{Sim}="2"$ (for instance “110” input pattern) and the input pattern is “111”, the $\text{Sum}$ signal becomes “0” and “1”, respectively.

To implement the capacitors of the proposed circuit, high density CNCAPs [10] are used. Using a $3 \times C_2$ capacitor instead of three $C_2$ capacitors improves the performance of the circuit. Besides, it makes a significant decrease in the circuit area and number of interconnect wires in comparison with CNT-FA-1 and CNT-FA-2. The proposed design utilizes only 5 capacitors and 8 transistors.

### Simulation Results Analysis and Comparison

The Synopsys HSPICE circuit simulator has been used to simulate the Full Adders. For simulating CMOS circuits, 32nm CMOS technology has been used. In addition, for CNFET-based circuits, compact SPICE model, including nonidealities proposed in [20-22], has been used for simulations. This standard model has been designed for unipolar, MOSFET-like CNFET devices, in which each transistor may have one or more CNTs. This model also considers Schottky Barrier Effects, Parasitics, including CNT, Source/Drain, and Gate resistances and capacitances, and CNT Charge Screening Effects. The parameters of the CNFET model and their values, with brief descriptions, are shown in Table 1. All of the simulations have been done at room temperature at $0.5 \text{ V}$ and $0.65 \text{ V}$ supply voltages. The operating frequencies are $250 \text{ MHz}$ and $500 \text{ MHz}$. These designs are optimized in terms of PDP (Power Delay Product) [23] at $0.65 \text{ V}$ and $250 \text{ MHz}$ frequency with $2.1 \text{ fF}$ load capacitance. All the possible input transitions are checked and the delay parameter has been measured for each transition. The maximum delay has been chosen as the delay of the circuit. The power consumption parameter has been measured as the average power consumption during a long period of time. Finally, the PDP is calculated for making a
trade-off between speed and power consumption and general performance comparison.

### Table 1. CNFET Model Parameters

| Parameter | Description                                    | Value  |
|-----------|-----------------------------------------------|--------|
| $L_{ch}$  | Physical channel length                       | 32 nm  |
| $L_{eff}$ | The mean free path in the intrinsic CNT channel | 100 nm |
| $L_{so}$  | The length of doped CNT source-side extension region | 32 nm  |
| $L_{sd}$  | The length of doped CNT drain-side extension region | 32 nm  |
| $K_{die}$ | The dielectric constant of high-k top gate dielectric material | 16     |
| $T_{ox}$  | The thickness of high-k top gate dielectric material | 4 nm   |
| $C_{sub}$ | The coupling capacitance between the channel region and the substrate | 20 pF/m |
| $E_{fi}$  | The Fermi level of the doped S/D tube | 6 eV   |

The simulation results of CCMOS, Bridge-CMOS, Hybrid1, Hybrid2, TG, CNT-FA-1, CNT-FA-2 and the proposed design in different situations are shown in Table 1. At 0.5V supply voltage, the proposed design is approximately 85.76%, 88.97%, 79.64%, 80.14%, 73.06%, 36.64% and 68.52% faster than CCMOS, Bridge-CMOS, Hybrid1, Hybrid2, TG, CNT-FA-1 and CNT-FA-2. The PDP of the proposed design is 79.47%, 82.45%, 67.4%, 70.46%, 60.55%, 52.3% and 46.5% better than CCMOS, Bridge-CMOS, Hybrid1, Hybrid2, TG, CNT-FA-2 and CNT-FA-1 respectively. It is 68%, 78.8%, 66.21%, 64.72%, 54.11%, 40.43% and 8.2% faster than CCMOS, Bridge-CMOS, Hybrid1, Hybrid2, TG, CNT-FA-2 and CNT-FA-1 at 0.65 V supply voltage.

The proposed design has the best PDP and delay in comparison with other cells in Table 2 at all supply voltages. Figure 5 shows PDP diagrams in the considered conditions. It can be inferred from the charts that at 250 MHz and 500 MHz frequencies the PDP of the proposed design is less than that of the previous designs. This is due to the shorter critical path of the proposed circuit, which leads to shorter propagation delay and lower number of utilized devices and circuit internal nodes resulting in less capacitance and lower average power consumption.

Figure 6 shows the waveforms of the proposed design at 0.5 V supply voltage. This design performs very well at low supply voltages and high frequencies and has full swing.
An important attribute of the circuits which should be taken into account is their immunity to the ambient temperature variations [24]. As a result, the circuits have been simulated in a vast range of temperatures, from $0^\circ$C up to $70^\circ$C, to evaluate their sensitivity to temperature noises. The results of this experiment, at $0.65$ V supply voltage, $250$ MHz and with $2.1$ fF load capacitance, are plotted in Fig. 7. It can be inferred from Fig. 7 that the proposed design has acceptable functionality and performance in a vast range of temperatures and is superior in terms of PDP, in comparison with the other circuits at all temperatures.

### Conclusion

This paper has proposed a novel high-speed and low-voltage CNFET-based Full Adder circuit based on Minority function for nanotechnology. This design has rail-to-rail output signals and works properly at low voltages. In order to evaluate its performance some conventional and state-of-the-art $32$ nm
CMOS and CNFET-based Full Adder designs are simulated. The simulation results indicate that significant improvements in terms of speed and energy efficiency are achievable in different test conditions by utilizing the proposed design.

The authors would like to thank Dr. Belmond Yoberd for his literature contribution.

Received 9 May 2010; accepted 18 June 2010; published online 30 June 2010

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Low-energy electronic states of carbon nanocones in an electric field

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The low-energy electronic states and energy gaps of carbon nanocones in an electric field are studied using a single-π-band tight-binding model. The analysis considers five perfect carbon nanocones with disclination angles of 60°, 120°, 180°, 240° and 300°, respectively. The numerical results reveal that the low-energy electronic states and energy gaps of a carbon nanococone are highly sensitive to its geometric shape (i.e. the disclination angle and height), and to the direction and magnitude of an electric field. The electric field causes a strong modulation of the state energies and energy gaps of the nanocones, changes their Fermi levels, and induces zero-gap transitions. The energy-gap modulation effect becomes particularly pronounced at higher strength of the applied electric field, and is strongly related to the geometric structure of the nanocone.

Keywords: Low-energy electronic states; Carbon Nanocones; Electric field

Citation: Jun-Liang Chen, Ming-Horng Su, Chi-Chuan Hwang, Jian-Ming Lu and Chia-Chang Tsai, “Low-energy electronic states of carbon nanocones in an electric field”, Nano-Micro Lett. 2, 121-125 (2010). doi:10.5101/nml.v2i2.p121-125

The properties and potential applications of carbon-related nanometer-size materials have attracted intensive interest in recent years. Of these various materials, carbon nanotubes play a particularly crucial role in the field of nano-material science and technology. Since the observation of multiwalled carbon nanotubes by Iijima [1], many carbon nanostructures have identified, such as carbon tori [2], carbon nanohorns [3], and carbon nanocones [4], etc. A graphite sheet can be notionally divided into six equivalent wedges by choosing one of its hexagon centers through each of its corners. A nanocone can then be formed by removing one or more of these wedges from the graphite sheet and rolling up the remainder. Nanocones are identified by their disclination angle $\alpha$ where this angle corresponds to the angle of the part removed from the sheet before the rolling process. The surface of a nanocone can be regarded as a hexagonal network containing pentagonal defects. The growth process of carbon nanocones compared to those of carbon nanotubes and $C_{60}$ was studied by Ge and Sattler [4]. The results showed that perfect carbon nanocones have one of five possible open apex angles, i.e. 123.6°, 86.6°, 60°, 38.9° and 19.2° corresponding to their disclination angles of 60°, 120°, 180°, 240° and 300°, respectively.

Many theoretical [5-10] and experimental studies [11-14] of the geometric and electronic properties of carbon nanocones or nanotube tips have been revealed over the past decade. In general, the results have shown that the electronic structure, e.g. the electronic states, energy gaps and density of states, are highly sensitive to the symmetry of the edge sites at the open apex and to the curvature effect. However, relatively few studies have investigated the effect of an electric field on the electronic structures of carbon nanocones. It is known that an electric field can significantly affect the electronic properties of

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carbon-related systems such as carbon nanotubes [15-21],
carbon tori [22], and layered graphite [23]. Hence, it is
reasonable to speculate that the energy gap of a carbon
nanocone will also be modulated under the effects of a uniform
electric field. Accordingly, in this study, a tight-binding model
is employed to investigate the changes, induced by a uniform
electric field, on the low-energy electronic structures of perfect
carbon nanocones.

The schematic diagram of a carbon nanocone is shown in
Fig. 1. The current investigations consider carbon nanocone
structures with disclination angles α of 60°, 120°, 180°, 240°
and 300°, respectively. Each of these nanocones is comprised a
similar number N of carbon atoms. The C–C bond length
aC–C of this conical system is approximately 1.42 Å, and
the open base of each nanocone is terminated by hydrogen atoms.
The single-π-band tight-binding model is used to calculate the
low-energy electronic states. In this model, the 2pπ orbitals
can describe completely the π-electronic states so as to dominate
exactly the low-energy electronic properties. However, the σ
bands are omitted because they are far from the Fermi energy EF.
In present analysis, the interaction between two
nearest-neighbor carbon atoms is considered and the magnitude
of this interaction, γ0, is assumed to be 3.033 eV [24]. When an
electric field E is applied, the low-energy electronic state of the
nanocones is modulated drastically. However, it is assumed that
E has no effect on the geometric structure of the nanocones and
thus on the parameter γ0. Furthermore, due to the screen effect,
E is regarded as an effective field, that is, it changes only the
on-site potential of the carbon atoms.

![FIG 1. Schematic diagram of carbon nanocone showing Cartesian coordinate system and a uniform electric field, E, applied at an incidence angle, αE, to the cone axis (z-axis).](http://www.nmletters.org)

The nearest-neighbor Hamiltonian is given by

\[
H = \sum_{i=1}^{N} \varepsilon_i(E) c_i^\dagger c_i + \sum_{i \neq j=1}^{N} (-\gamma_0) c_i^\dagger c_j
\]  

(1)

where \(\varepsilon_i(E)\) are the unperturbed on-site potentials induced by E, and \(c_i^\dagger(c_j)\) the creation (annihilation) operators of Fermions. The Hermitian matrix representation of this Hamiltonian is built from the subspace spanned by the N basis wavefunctions of 2pπ orbitals. For convenience, the Cartesian coordinate is used in current computations and the position of each atom is denoted as \((x_i, y_i, z_i)\), \(i = 1, \ldots, N\). The origin of the coordinate is located at the center of the carbon nanocone (see Fig. 1). The symmetry axis of the carbon nanocone is parallel to the \(\hat{z}\)-axis of the coordinate. The distance \(\Delta_{ij}\) between the i-th and j-th carbon atoms is given by

\[
\Delta_{ij} = \sqrt{(\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2}
\]

where \(\Delta x = |x_i - x_j|\), \(\Delta y = |y_i - y_j|\) and \(\Delta z = |z_i - z_j|\).

If E is absent, the elements of the Hamiltonian matrix are given by

\[
H_{ij} = \begin{cases} 
-\gamma_0 & \Delta_{ij} = a_{CC} \\
0 & \text{otherwise} 
\end{cases}
\]

(2)

However, when the electric field is applied, the on-site energies of the carbon nanocone will be changed. In present
analysis, the electric field is assumed to be

\[E = E_0 \cos \alpha_E \mathbf{e}_z + E_0 \sin \alpha_E \mathbf{e}_x = E_1 + E_\perp\]

Where, E is the strength of the electric field and in the unit of \(\gamma_0/\text{Å}\). Meanwhile, \(\alpha_E\) is the angle between the electric field
direction and the \(\hat{z}\)-axis, and \(\mathbf{e}_x\) (\(\mathbf{e}_y\)) is the unit vector in \(\hat{x}\)-(\(\hat{y}\))-axis. After applying the electric field, the diagonal elements of the Hamiltonian matrix vary from zero to

\[H_{ii} = \varepsilon_i(E) = -E_0 z_i \cos \alpha_E - E_1 x_i \sin \alpha_E
\]

(3)

The electronic state energies of carbon nanocones are obtained by diagonalizing the N by N Hamiltonian matrix
[25-28], and are expressed as \(E^{(i)}(M, \mathbf{E})\), where \(M\), from 1 to
N, represents the discrete state, and \(\mathbf{E}\) \((\mathbf{U})\) corresponds to the
unoccupied (occupied) states. Note that an energy gap, \(E_g\), may
exist between the highest occupied molecular orbital (HOMO)
state and the lowest unoccupied molecular orbital (LUMO)
state.

The present analysis commences considering the effects on
the low-energy electronic states of the carbon nanocones due to
an electric field whose direction is parallel to the symmetry axis
of the cone, i.e. \(\mathbf{E} = E_0 \mathbf{e}_z\) and \(\alpha_E = 0^\circ\). Figure
2(a)-(e) presents the π-electronic states corresponding to the
2pπ orbitals of the five nanocones. Note that the value of Fermi
energy is set to be zero \((E_F = 0)\) in the computations. At \(E = 0\), it
is observed that the lowest electronic states, which are close to $E_F$, are symmetric, while the other states are non-symmetric. However, as $E$ increases, the electronic states are drastically modulated and state crossings take place at $E_F = 0$ indicating the occurrence of zero-gap transitions (ZGTs), i.e. a change in the energy gap from a finite value to zero, or vice versa. It is revealed that the ZGTs occur more frequently at larger $E$ values.

The nanocone with the largest disclination angle, $\alpha$, has the greatest height between the apex and the base, and the magnitude of the on-site potential induced by $E$ is also the highest. As a result, a more drastic modulation of the electronic states takes place. In other words, as the strength of the applied electric field or the disclination angle increases, the extent of the modulation effect also increases. Significantly, the HOMOs and LUMOs of the carbon nanocones are symmetric to one another about $E_F$ at larger $E$ values. Finally, Fig. 2(f) shows that the Fermi energies of these five systems increase almost linearly with increasing $E$ (larger $E$ indicates the increment of the on-site potential $e_i(E)$). Overall, the results presented in Fig. 2 demonstrate that the low-energy electronic states and Fermi energies of carbon nanocones are strongly dependent on the nanocone geometry.

Sequentially, we want to investigate the effect of the electric field on the energy gaps of the carbon nanocones. Figure 3(a) shows the influence of $E$ on the energy gaps of the five carbon nanocones. The electric field strength $E$ is increased from zero to 0.1 $\gamma_0$/Å. It is shown that, in the absence of the electric field, the carbon nanocones with $\alpha = 60^\circ$, 120$^\circ$, and 180$^\circ$ are semiconducting, while those with $\alpha = 120^\circ$, 180$^\circ$, and 300$^\circ$ are metallic. As $E$ increases to 0.1 $\gamma_0$/Å, the energy gaps are strongly modulated, and ZGTs take place. It is observed that the ZGTs occur more frequently when a nanocone has a larger $\alpha$ angle and is emitted at higher strength of $E$; meanwhile, we know that both larger value of $\alpha$ and of $E$ will increase the strength of the on-site potential. Figure 3(b) illustrates the influence of incidence angles $\alpha_E$ of an electric field on the energy gap of the carbon nanocone with a disclination angle of 60$^\circ$. At $\alpha_E = 0^\circ$, two ZGTs occur at $E < 0.05 \gamma_0$/Å. However, as the direction of the electric field moves away from the $\hat{z}$-axis,
the energy-gap modulation effect becomes more pronounced. It is observed that the original ZGTs at $E < 0.05 \gamma / \text{Å}$ vanish at larger values of $\alpha_e$. For this particular nanocone $\alpha = 60^\circ$, the opening angle is 123.6°, i.e. the radius of the open edge is greater than the height of this nanocone. Therefore, the variation of the on-site potential in the radial direction is larger than that in the axial direction.

![Graph of $E_g(\alpha)$ vs $E (\gamma / \text{Å})$](image1)

![Graph of $E_g(\alpha)$ vs $L (\text{Å})$](image2)

**FIG. 3.** (a). Influence of $E_{\text{eq}}$ on electric-field-dependent energy gaps of carbon nanocones with disclination angle of $\alpha = 60^\circ$, 120°, 180°, 240° and 300°, respectively. (b). Influence of electric-field incidence angle on the energy gap of the carbon nanocones with $\alpha = 60^\circ$ and $N = 1080$.

In a previous study [29], the authors showed that the energy gaps of a finite-length carbon nanotube were highly sensitive to its length. Therefore, the influence of the nanocone height, $L$, on the energy gaps is investigated in current study. Figure 4 illustrates the variation of the energy gap with $L$ for a nanocone with disclination angle $\alpha = 240^\circ$ as a function of the strength and the direction of an applied electric field. In the absence of an electric field, the energy gap oscillates randomly with increasing $L$ and gradually approaches zero at $L > 50$ Å. The decay-like characteristic evident in Fig. 4 is very similar to that observed in finite-length carbon nanotubes with different cap configurations [29]. At $E = 0.01 \gamma / \text{Å}$, the energy-gap modulation effect is very weak in nanocones with any disclination angle when $L$ is small. However, as $L$ increases, the energy-gap modulation effect of the electric field increases significantly. Moreover, the change in the energy gap at $\alpha_e = 90^\circ$ is more evident than that at $\alpha_e = 0^\circ$. As a result, it is shown that the energy-gap modulation effect is sensitive to changes in both the height of the carbon nanocone and the direction and strength of the electric field.

![Graph of $E_g(L)$ vs $L (\text{Å})$](image3)

**FIG. 4.** Influence of nanocone height ($L=6$–$48\text{Å}$) on energy gap of the carbon nanocone with $\alpha=240^\circ$ and $N=1056$ for $E=0 \gamma / \text{Å}$ and $E=0.01 \gamma / \text{Å}$ which applied with the incidence angles of $0^\circ$, $30^\circ$, $60^\circ$ and $90^\circ$, respectively.

A single-$\pi$-band tight-binding model is used in this study to investigate the effects of an electric field on the electronic properties of perfect carbon nanocones with disclination angle of $60^\circ$, $120^\circ$, $180^\circ$, $240^\circ$ and $300^\circ$, respectively. The results reveal that the low-energy electronic states, energy gap, and Fermi energy are highly sensitive to the geometric structure of the nanocone and to both the strength and direction of the applied electric field. The electric field causes a modulation of the electronic states and energy gaps of the nanocones, prompts ZGTs, and induces an almost linear change about the Fermi energy. Significantly, the HOMO and LUMO are symmetric to one another about the Fermi energy irrespective of the strength of the electric field. The present results provide further insights into the fundamental properties of conical finite-size systems in an electric field.

The authors wish to thank Professor Yun-Che Wang, (NCKU, Taiwan) for valuable assistances and suggestions. This study was supported in part by the National Science Council of Taiwan under Grant Nos. NSC 96-2221-E-492-007-MY3 and NSC 98-2221-E-006-131-MY3. We also acknowledged the National Center for Theoretical Science (NCTS) in Taiwan.
Received 14 April 2010; accepted 19 Jun 2010; published online 6 July 2010.

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Performance comparison of zero-Schottky-barrier and doped contacts carbon nanotube transistors with strain applied

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Atomistic quantum simulation is performed to compare the performance of zero-Schottky-barrier and doped source-drain contacts carbon nanotube field effect transistors (CNTFETs) with strain applied. The doped source-drain contact CNTFETs outperform the Schottky contact devices with and without strain applied. The off-state current in both types of contact is similar with and without strain applied. This is because both types of contact offer very similar potential barrier in off-state. However, the on-state current in doped contact devices is much higher due to better modulation of on-state potential profile, and its variation with strain is sensitive to the device contact type. The on/off current ratio and the inverse subthreshold slope are better with doped source-drain contact, and their variations with strain are relatively less sensitive to the device contact type. The channel transconductance and device switching performance are much better with doped source-drain contact, and their variations with strain are sensitive to device contact type.

Keywords: Zero-Schottky-barrier; Doped contact; Strain; Inverse subthreshold slope; Intrinsic cut-off frequency

Citation: Md. Abdul Wahab and Khairul Alam, “Performance comparison of zero-Schottky-barrier and doped contacts carbon nanotube transistors with strain applied”, Nano-Micro Lett. 2, 126-133 (2010). doi: 10.5101/nml.v2i2.p126-133

Carbon nanotube (CNT) is a fascinating material that shows metallic or semiconducting behavior depending on its radius and chirality [1-7]. CNTs can withstand very large mechanical strains [8], and have extremely high Young's modulus [9]. The strain has significant effects on the electronic properties of CNTs [3-7,10-14]. Maiti et al. [14] have shown that strain can change the conductance of a zigzag nanotube by several orders of magnitude. The pioneer experiment by Tombler et al. [15] shows that high strain (~3%) can change the conductance of a metallic single-walled nanotube by two orders of magnitude. In that experiment, strain was applied to a suspended multi-walled CNT using atomic force microscope (AFM) tip. Strain can open up a band gap in metallic CNTs, and can modify the band gap of semiconducting CNTs [16]. Small band gap semiconducting or quasi-metallic nanotubes exhibit the largest changes in resistance and piezo-resistive gauge factors, and they can be used as nanoscale pressure sensors [17].

While the study of strain effects on electronic and mechanical properties of CNTs shows significant progress, strain engineering in CNT based devices is still in early stage. Single-walled carbon nanotube devices have been fabricated on elastomeric polydimethylsiloxane (PDMS) substrates [18]. In those devices, strain has been applied to modulate their electronic properties. The conductance of a suspended multi-walled CNT has been measured by applying strain using AFM tip [19]. The strain effects on the performance of ballistic Schottky-barrier carbon nanotube transistors have been theoretically studied [20].

In this paper, we compare the performance of ballistic zero-Schottky-barrier and doped source-drain contacts carbon
nanotube transistors with strain applied. Performance comparison between Schottky and doped contacts CNTFETs has been carried out before without strain [21,22]. Our simulation model self-consistently solves the non-equilibrium Green’s function (NEGF) equations for charge density and the two dimensional Poisson’s equation in cylindrical coordinates for electrostatics. The CNT is modeled using π-orbital of carbon atom. The doped contact devices outperform the Schottky contact CNTFETs. The variation of off-state current with strain is not sensitive to the contact type; however, the magnitude of on-state current variation with strain is sensitive to device contact type. This is because the potential barrier in off-state for both types of contact is almost same, and therefore, the off-state current is not sensitive to the contact type with and without strain. However, the on-state current in Schottky contact devices is limited by the Schottky barrier, and the gate does not modulate much the potential profile when the potential under the gate goes below the source Fermi level. On the other hand, the gate modulation of potential profile is relatively larger in doped contact devices even after the source-channel flat band condition, and therefore, the on-state current in doped contact devices is much higher. The strain changes the band gap that changes the modulation of on-state band profile. This effect is higher in doped contact devices. The on/off current ratio and the inverse subthreshold slope are better in doped contact devices, and their variations with strain are not much sensitive to device contact type. The switching performance of doped contact devices is better, and its variation with strain is sensitive to device source-drain contact type.

SIMULATION MODEL

The simulation model uses a self-consistent solution between electrostatics and charge density. For a coaxially gated CNTFET, we obtain electrostatic potential by solving two-dimensional Poisson’s equation in cylindrical coordinates \( r, \phi, z \)

\[
\frac{\partial^2 V}{\partial r^2} + \left[ \frac{1}{r} + \frac{1}{\epsilon_e \partial \phi_e} \right] \frac{\partial V}{\partial r} + \frac{\partial^2 V}{\partial \phi_e^2} = -\frac{\rho}{\epsilon_e}.
\]  

The Poisson’s equation, Eq. (1), is discretized using finite difference, and is solved by standard Newton-Raphson method. The potential is fixed to \( V_{GS} - \Phi_e/q \) at the gate electrode. For Schottky contact, potential is fixed to \( -\Phi_e/q \) at the source electrode and to \( V_{DS} - \Phi_e/q \) at the drain electrode. Here, \( V_{GS} \) and \( V_{DS} \) are the gate to source and drain to source voltages, and \( \Phi_e \) and \( \Phi_d \) are the work functions of gate, source, and drain metallizations. For doped source-drain contacts, the axial component of electric field is set to zero at the source and drain ends. The radial component of electric field is set to zero along the exposed surface of dielectric.

The CNT is modeled using π-orbital basis of carbon atom. When strain is applied, we assume that the on-site energy does not change, and the hopping parameter changes following Harrison’s formula [23] \( V_{pp} = V^0_{pp}(r_0/r)^2 \). Here, \( V^0_{pp} \) and \( r_0 \) are the hopping parameter and the carbon-carbon bond length, respectively, of the unstrained CNT, and \( r \) is the bond length of strained CNT. With uniaxial strain applied, the axial, \( r_a \), and the circumferential, \( r_c \), components of a carbon-carbon bond are calculated by the following equations [5]

\[
\begin{align*}
&\ t_a = (1 + e_a) r_0, \\
&\ t_c = (1 + e_c) r_0. \\
&\ \end{align*}
\]

(2)

Here, axial strain, \( e_a \), and circumferential strain, \( e_c \), are related via Poisson’s ratio \( v = -e_a/e_c \), and \( r_0 \) and \( r_0 \) are the axial and circumferential components, respectively, of the unstrained carbon-carbon bond. A Poisson’s ratio value of 0.2 is used in our simulation [7,20]. For torsional strain, the circumferential component of the carbon-carbon bond is modified as \( r_c = r_0 + \tan(\gamma) r_0 \) where, \( \gamma \) is the shear strain. The Hamiltonian parameter values are taken from Ref. [24].

For charge density calculation, we use recursive Green’s function (RGF) algorithm [25,26] to solve NEGF equations. The charge density at the \( L^{th} \) atomic layer is calculated from

\[
\rho_L = (2e) \int \frac{dE}{2\pi} \text{tr} \left[ \left( f_S A^L_{L,L} + f_D \left( A^L_L - A^L_{L,L} \right) \right) \right],
\]

Where, the factor 2 includes spin degeneracy, \( e \) is the electronic charge, tr is the trace over the atomic orbitals, and \( f_S \) and \( f_D \) are the source and drain Fermi functions, respectively. The full spectral function is calculated from \( A^L_L = G_{LL}^{\text{tg}} \Gamma_L G_L^{\text{tg}} \) and the left spectral function from \( A_{L,L}^L = G_{L}^{\text{tg}} \Gamma_L G_L^{\text{tg}} \). The Green’s function is defined as \( G(E-H-S)^{-1} \), and the broadening function \( \Gamma \) is negative twice the anti Hermitionian component of self energy \( S \). The self energies are \( \Sigma_{1,1} = -iI_{1,0} \) and \( \Sigma_{N,N} = -iI_{N,N+1} \) for the Schottky contact devices [26,27], and \( \Sigma_{1,1} = I_{1,0}g_{0}p_{0,1} \) and \( \Sigma_{N,N} = iR_{N,N+1}R_{N+1,N}g_{N+1,N+1} \) for the doped contact devices [28]. Here, \( I, r \)’s are the coupling matrices, and \( g_{0,0} \) and \( g_{N+1,N+1} \) are the
surface Green’s functions. We use decimation method [29,30] to calculate the surface Green’s function
\[
A_n = A_{n-1} (E - H_{n-1})^{-1} A_{n-1}
\]
\[
B_n = B_{n-1} (E - H_{n-1})^{-1} B_{n-1}
\]
\[
H'_n = H'_{n-1} + A_{n-1} (E - H_{n-1})^{-1} B_{n-1}
\]
\[
H_n = H_{n-1} + A_{n-1} (E - H_{n-1})^{-1} B_{n-1} + B_{n-1} (E - H_{n-1})^{-1} A_{n-1}.
\]
(4)

Here, \( n \) is the iteration number. Iterations are repeated until \( A_n \) and \( B_n \) are small enough so that the nearest neighbor coupling can be disregarded. Then the surface Green’s function can be obtained from \( g'(E) = (E - H'_n)^{-1} \). For \( g(t,0) \), the iteration is started with \( A_0 = t_{1,0} \) and \( B_0 = t_{0,0} \). For \( g(N,1,1) \), the iteration is started with \( A_0 = t_{0,1} \) and \( B_0 = t_{1,0} \). In both cases, the matrix \( H_0 \) is the unit cell Hamiltonian of the carbon nanotube, and \( H'_0 = H_0 \).

The coherent drain current is calculated from
\[
I_D = \frac{2e}{h} \int dE (E)(f_s - f_D).
\]
Where, \( h \) is Planck’s constant, and the transmission is calculated from [25]
\[
T(E) = \text{tr} \left[ \Gamma_{1,1} \left( A_{1,1} - G_{1,1} \Gamma_{1,1} G_{1,1}^\dagger \right) \right].
\]
(6)

The self-consistent loop is started with an initial guess of the potential profile. We generate the initial profile following Ref. [31]. That is, the initial conduction band edge is a step profile with \( E_C = E_{CS} \) in the source region, \( E_C = E_{CS} + E_f/2 \) under the gate region, and \( E_C = E_{CS} - eV_{DS} \) in the drain region. Here, \( V_{DS} \) is the drain to source bias, \( e \) is the electronic charge, and \( E_{CS} \) is the conduction band edge relative to the source Fermi level and is calculated from the charge neutrality condition. However, for Schottky contact, the potentials are fixed at the gate, source, and drain terminals, and therefore, our initial potential profile is generated from the Laplace equation. The update profile for the next iteration of self-consistent loop is created using Anderson mixing scheme [32].

**NUMERICAL RESULTS AND DISCUSSIONS**

We simulate coaxially gated zero-Schottky-barrier and doped source-drain contacts CNTFETs. The device cross sections used for simulation are shown in Fig. 1. An \((n,0)\) zigzag CNT is used as the channel material. The devices have a gate length \( L_g \) of 10 nm and source and drain extensions \( L_{ox} \) and \( L_{ad} \) of 30 nm each. The gate oxide is SiO\(_2\) with thickness \( t_{ox} \) of 2 nm. Poisson solver uses an extended dielectric thickness \( t_{ox,ex} \) (or gate metal thickness) of 6 nm. For Schottky contact devices, the source and drain metal extensions \( L_{es} \) of 15 nm are included in Poisson solver to take care of the fringing electric fields. For the doped contact devices, the source and drain contacts are assumed to be uniformly doped. The gate metal is assumed to have the same work function value as the CNT has. For zero-Schottky-barrier contacts, the source and drain metal Fermi functions align with the conduction band of the CNT. Ballistic transport is assumed. We use both uniaxial and torsional strains in our simulation.

![Device cross sections for simulation](image)

**FIG. 1.** Device cross sections used for simulation. (a) zero-Schottky-barrier source-drain contacts. (b) doped source-drain contacts.

The band gap variations with uniaxial and torsional strains of \((13,0)\) and \((14,0)\) CNTs that cover two families of CNTs are shown in Fig. 2. The other family, mod \((n,m,3) = 0\), is represented as negative and positive strains, respectively.

![Band gap variation](image)

**FIG. 2.** The band gap variations with (a) uniaxial and (b) torsional strains of \((13,0)\) and \((14,0)\) CNTs. Here, compressive and tensile uniaxial strains are represented as negative and positive strains, respectively.
not discussed in this study because it has zero band gap at no strain. All the CNTs that have mod (n-m,3) = 1 will show the band gap variation similar to (13,0) and similar to (14,0) if mod (n-m,0) = 2 [5,20]. The band gap of the (13,0) CNT with 2% uniaxial strain is about 25% larger than that of the unstrained one. For the (14,0) CNT, this gap is about 26% smaller than that of the unstrained CNT at 2% uniaxial strain. A 6° of torsional strain increases the band gap of the (13,0) CNT by 19%, and decreases the band gap of the (14,0) CNT by 23%. Uniaxial strain on a CNT may either increase or decrease the band gap by applying either tensile or compressive strain. Torsional strain however only increases the band gap of mod (n-m,3) = 1 CNTs, and decreases the band gap of mod(n-m,3) = 2 CNTs regardless of whether the torsional angle is positive or negative [20].

From hereon, we will use (13,0) CNT as the channel material to study performance of CNTFETs with strain. The other family shows the opposite behavior of performance metrics with strain compared to the (13,0) devices due to the opposite nature of band gap variation, Fig. 2. The variations of off-state current with strain for (13,0) CNTFETs are shown in Fig. 3. The shape of the off-state current versus strain curves of Schottky-barrier (13,0) CNTFET follows the shape of mod (n-m,3) = 1 family reported before [20]. The off-state current in our study is the drain current at zero gate bias with $V_{DS} = 0.5V$. The off-state current of both zero-Schottky-barrier and doped contact devices is almost same at no strain. The off-state current improves with tensile uniaxial strain for (13,0) CNT channel. The rotational strain improves the off-state current of (13,0) CNT channel. Note that results for positive angles of torsional strain are shown because the band gap variation with torsional strain is symmetric with positive and negative angles. The physics behind the off-state current variation with strain is the modulation of band gap (see Fig. 2) with strain. The off-state current improves with the type of strain that increases the band gap. This is because, with intrinsic channel, the off-state potential barrier height and width increase with larger band gap as shown in Fig. 4. The increased height and width of the barrier reduces the off-state current, mainly the tunneling component of current. The off-state currents are 6.487×10^{-5} μA, 9.9×10^{-7} μA, and 3×10^{-8} μA for the (13,0) CNT devices with zero-Schottky-barrier contact at a 2% compressive strain, at no strain, and at a 2% tensile strain, respectively. These values for the doped contact devices are 1.4×10^{-4} μA, 1.25×10^{-5} μA, and 2.6×10^{-8} μA, respectively. So the strain effect on off-state current is not much sensitive to the contact type. This is also true for the torsional strain.

![FIG. 3. The off-state current versus strain. The SB means zero-Schottky-barrier and DP means doped source-drain contacts.](image)

![FIG. 4. Conduction band profiles vs channel position in (a) off ($V_{DS} = 0.5 V$ and $V_{GS} = 0 V$) state and (b) on ($V_{DS} = 0.5 V$ and $V_{GS} = 0.5 V$) state. Here, SB means zero-Schottky-barrier, and DP means doped source-drain contacts devices. The channel is a (13,0) CNT. The solid lines are the band profiles of unstrained CNT channel, and the dashed lines are the band profiles of 2% tensile strained CNT channel.](image)
because the on-state potential barrier height reduces with the type of strain that reduces the band gap. This is evident from the band profiles shown in Fig. 4. The on-state current at no strain is much higher in doped contact devices compared to the Schottky contact devices. The on-state currents for Schottky contact devices are 1.78 μA, 0.865 μA, and 0.47 μA at a 2% compressive strain, at no strain, and at a 2% tensile strain, respectively. These values for the doped contact devices are 21.6 μA, 9.6 μA, and 2.23 μA, respectively. While the improvement of on-state current for the Schottky contact device is from 0.865 μA to 1.78 μA at a 2% compressive strain, this is from 9.6 μA to 21.6 μA for the doped contact device. So the strain effect on on-state current is sensitive to the contact type when current magnitude is compared. However, the percentage change of on-state current with strain is less sensitive to the device contact type. This is also true for the torsional strain.

The on/off current ratio versus uniaxial and torsional strains with Schottky and doped contacts are shown in Fig. 6. The on/off current ratio is better in doped contact devices. The change in on/off current ratio with strain is slightly sensitive to the device contact type, especially in case of torsional strain. This is because the off-state current variation with strain is not sensitive to the contact type, and this sensitivity of on-state current is not significant. For the Schottky contact CNTFETs, the on/off current ratios are 2.74×10^5, 7.71×10^5, and 8.4×10^5, respectively. The on/off current ratios are 9.96×10^5 and 5.64×10^7 for Schottky contact and doped contact, respectively, with 6° torsional strain.

The variations of inverse subthreshold slope, defined as $S = (\partial \log I_D / \partial V_{GS})^{-1}$, with strain are shown in Fig. 7. The inverse subthreshold slope improves with tensile and torsional strain.

**FIG. 5.** The on-state current versus strain. Here, SB means zero-Schottky-barrier contact and DP means doped contact.

**FIG. 6.** The on/off current ratio versus strain. Here, SB means zero-Schottky-barrier contact and DP means doped contact.

1.54×10^5, 7.71×10^5, and 8.4×10^5, respectively. The on/off current ratios are 9.96×10^5 and 5.64×10^7 for Schottky contact and doped contact, respectively, with 6° torsional strain.

The variations of inverse subthreshold slope, defined as $S = (\partial \log I_D / \partial V_{GS})^{-1}$, with strain are shown in Fig. 7. The inverse subthreshold slope improves with tensile and torsional strain.
strains. The inverse subthreshold slope is better in doped contact devices, and its change with strain is slightly sensitive to device contact type, especially with torsional strain. The inverse subthreshold slopes are 71.36 mV/dec, 61.4 mV/dec, and 60.30 mV/dec for Schottky contact and 69.78 mV/dec, 60.68 mV/dec, and 60.03 mV/dec for doped contact at a 2% compressive strain, at no strain, and at a 2% tensile strain, respectively. The inverse subthreshold slopes are 60.21 mV/dec and 60.0 mV/dec at 6° torsional strain for Schottky contact and doped contact, respectively.

Finally we compare the switching performance, namely the channel transconductance $g_m$, the intrinsic switching delay $\tau_s$, and the intrinsic unity current gain frequency $f_T$. For this the gate capacitance is calculated from

$$C_g = 2\pi R \int_0^{L_s} \frac{\delta D}{\delta V_g} dz + 2\pi \int_{\alpha_1}^{\alpha_0} r dr \frac{\delta D}{\delta V_g}, \quad (7)$$

Where, $R$ is the radius of the dielectric covering $\epsilon_\alpha$. The first integral takes care of the fluxes emanating from the bottom surface of the gate metal, and the second integral takes care of the fluxes emanating from the two sides of the gate metal facing to the source and drain. This gives the total gate capacitance $C_g = C_{gs} + C_{gd}$ which includes the effects of fringing electric fields directly from the gate metal to the source and to the drain. The intrinsic switching delay is calculated from $\tau_s = C_{gs} I_{on}/V_{DD}$ and the intrinsic unity current gain frequency from $f_T = g_m/2\pi C_g$, where, the transconductance is computed from $g_m = \partial I_D/\partial V_{GS}$ at $V_{GS} = V_{DD}$.

The on-state transconductance for both types of contact are shown in Fig. 8. The transconductance improves with compressive strain. This dependency is opposite for tensile strain. This change has a clear relationship with the change in band gap with uniaxial and torsional strain. The $g_m$ increases with the type of strain that reduces the band gap. The transconductance of doped contact CNTFETs is much higher than that of Schottky contact devices. The values of $g_m$ are 5.3 $\mu$S, 4.5 $\mu$S, and 2.65 $\mu$S with Schottky contact and 116.22 $\mu$S, 88.23 $\mu$S, and 32.08 $\mu$S with doped contact at a 2% compressive strain, at no strain, and at a 2% tensile strain, respectively. The $g_m$ reduces with torsional strain. The values of $g_m$ are 2.9 $\mu$S and 43.78 $\mu$S at a torsional strain of 6° for Schottky contact and doped contact, respectively. In terms of magnitude change of $g_m$ strain has significant sensitivity to the device contact type. However, when the percent change is compared, this sensitivity may not be significant.
Torsional strain degrades the switching delay. The intrinsic switching delays are 0.1689 ps, 0.3053 ps, and 0.5309 ps with zero-Schottky-barrier contact at a 2% compressive strain, at no strain, and at a 2% tensile strain, respectively. These values for the doped contact devices are 0.0362 ps, 0.0664 ps, and 0.2017 ps, respectively. The intrinsic switching delays are 0.4892 ps and 0.1396 ps for zero-Schottky-barrier contact and doped contact, respectively, at 6° torsional strain. Here, also the doped contact CNTFETs outperforms the zero-Schottky-barrier CNTFETs. The switching frequency improves with the type of strain that reduces the band gap. The intrinsic switching frequencies are 1.4035 THz, 1.2699 THz, and 0.8435 THz with zero-Schottky-barrier at a 2% compressive strain, at no strain, and at a 2% tensile strain, respectively. For the doped contact devices, they are 11.8574 THz, 11.0137 THz, and 5.6739 THz, respectively. The intrinsic switching frequencies are 0.8735 THz and 7.492 THz for zero-Schottky-barrier and doped contact, respectively, at 6° torsional strain.

CONCLUSION

Performance of zero-Schottky-barrier and doped source-drain contacts carbon nanotube transistors is compared using a π-bond atomistic quantum simulation for different types of strain. The doped source-drain contact transistor has better performance with and without strain applied. The variations of on-state current and switching performance with strain are sensitive to the device contact type. However, strain effect on off-state current, on/off current ratio, and inverse subthreshold slope is almost insensitive to the device contact type.

Received 30 May 2010; accepted 22 June 2010; published online 6 July 2010

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Preparation and growth mechanism of nickel nanowires under applied magnetic field

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Nickel nanowires with large aspect ratio of up to 300 have been prepared by a hydrazine hydrate reduction method under applied magnetic field. The diameter of nickel nanowires is about 200 nm and length up to 60 μm. The role of magnetic field on the growth of magnetic nanowires is discussed and a magnetic nanowire growth mechanism has been proposed. Nickel ions are firstly reduced to nickel atoms by hydrazine hydrates in a strong alkaline solution and grow into tiny spherical nanoparticles. Then, these magnetic particles will align under a magnetic force and form linear chains. Furthermore, the as-formed chains can enhance the local magnetic field and attract other magnetic particles nearby, resulting finally as linear nanowires. The formation and the size of nanowires depend strongly on the magnitude of applied magnetic field.

Keywords: Nanowire growth mechanism; Nickel nanowires; Magnetic-field assisted synthesis

Citation: J. Wang, L. Y. Zhang, P. Liu, T. M. Lan, J. Zhang, L. M. Wei, Eric Siu-Wai Kong, C.H. Jiang and Y.F. Zhang, “Preparation and growth mechanism of nickel nanowires under applied magnetic field”, Nano-Micro Lett. 2, 134-138 (2010). doi: 10.5101/nml.v2i2.p134-138

Morphological control in nanostructures has become a key issue in the preparation of electronic, photonic devices as well as functional materials [1,2]. In addition, much attention has been focused on one-dimensional (1-D) nanostructure such as nanorods, nanowires, nanofibers and nanochains due to their potential applications in nanodevices [3-5]. As a typical magnetic material, 1-D metallic Ni nanomaterial in uniform morphology and high purity has become increasingly mandatory for specific applications such as microwave absorbing materials, magnetic recording media, gas sensors, drug deliveries, commercial batteries and catalysts [6-12]. To date, much effort has been made to prepare Ni nanomaterial with 1-D structure. Template methods are the most common synthesis technique. For example, Yu et al. prepared nickel nanowire arrays in alumina templates by using a chemical electrodeposition method [13]. Zhang et al. fabricated nickel hollow fiber using natural silk as the template [14]. It is well known that template-based methods are not facile and in fact, it is difficult to synthesize a large amount of nanomaterials using the template-based route [15]. In comparison, chemical reduction approach is much simpler and having lower cost. Recently Niu et al. fabricated acicular nickel nanocrystallites with an average length of 10 μm and a diameter of about 200 nm, using PEG and CTAB surfactant in a sealed autoclave under an external magnetic field, under high temperature and pressure [16]. Although Gong et al. synthesized Ni nanowires under normal pressure, ethylene glycol was used as the solvent [17]. In recent years, our research group has reported the facile synthesis of Ni nanowires in aqueous ethanol solution [18,19]. This is a much more promising approach to synthesize magnetic nanowires in large scale since it is simple, low-cost, high yield, and environmentally friendly.

In previous work, we have reported the synthesis of Ni nanowires [18,19]. In this investigation, we studied the

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magnetic field dependence of the morphology as well as the formation process of Ni nanowires. A possible growth mechanism has been proposed. The method reported in this paper can be used to fabricate large-scale Ni nanowires, as well as other 1-D magnetic nanowires. The proposed mechanism may further shed light on the fabrication approach on magnetic nanowires with high quality.

Experimental Section

All chemical reagents in our experiments are analytical grade and are used without further purification. Nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) was dissolved in a solution composed of distilled water and ethanol. Then, hydrazine hydrate with concentration of 85% was injected and the pH value was adjusted to 13.7 by using 5 M sodium hydroxide (NaOH) solution. The as-prepared, blue transparent solution was transferred to a flask and kept at 50 °C for 10~30 min. A permanent NdFeB magnet was placed under the flask and different applied magnetic fields can be obtained by adjusting the distance between the magnet and the flask. In this investigation, the Ni nanowires were synthesized at a magnetic field of 0.5 T. The magnetic field was measured using a Gauss meter (Model SHT-4A). After the reaction was completed, the resulting grey-black, fluffy solid product floated on top of the solution surface and the solution became colorless and transparent. The product was collected and washed several times using distilled water and ethanol under an applied magnetic field and then dried in vacuum oven at 60°C for 12 h.

The size and surface morphology of Ni nanowires were investigated by emission scanning electron microscopy (SEM, Zeiss Ultra 55, Germany) at an accelerating voltage of 5 kV. The detailed microstructure of the nanowires was studied by a transmission electron microscopy (TEM, JEM-100CX, JEOL, Japan). X-ray diffraction pattern was measured by a 18 kW advanced X-ray diffractometer (D8 ADVANCE, Bruker, Germany) with Cu Kα radiation ($\lambda = 1.54056$ nm).

Results and Discussion

The role of the hydrazine hydrate as a reducing agent in the reaction was investigated. It was found that no grey-black products formed if hydrazine hydrate was absent even at high temperature of 80°C and strong magnetic field of 0.5 T. This indicates that hydrazine hydrate played a very important role in the reaction as a reducing agent. Moreover, it was found that the reaction efficiency strongly depended on the pH value of the solution. When pH value was 13.7, the reaction will complete within 30 min at 50°C. However, when the pH value was 13.0, no nanowires were produced until the reaction temperature was increased to 86°C. If the pH value was below 13.0, the reaction would not take place even at 100°C. Thus, choosing the proper pH value is essential on the synthesis of the nickel nanowires as described in this investigation. The important role of pH value on formation of Ni nanomaterials has also been discussed by other groups [20,21]. In addition, we found that higher reaction temperatures will accelerate the reaction processes, that is, it will need less time to complete the reaction at a higher temperature. At the selected reaction temperature of 50 °C at pH value of 13.7, the reaction time will be 30 min.

Figure 1a shows the SEM images of nickel nanowires prepared at 50°C, pH value of 13.7, the strength of the applied magnetic field of 0.5 T and the concentration of the Ni ions of 0.08 mol/L. It can be seen that the nanowires are uniform and the mean diameter is 200 nm and length of 60 μm. From the magnified image shown in Fig. 1b, one can see the nanowires are composed of nanoparticles in diameters from 20 to 60 nm. The surfaces of the nanowires are not smooth and there exist a lot of spiny-like particles.

The detailed structure of the nanowires was observed by TEM, as shown in Fig. 2a. It is obvious that the Ni nanowires are assembled to 1-D solid linear structure under an applied magnetic field. The magnetic field plays a very important role in the formation of 1-D nanostructure. Even if they were
ultrasonically treated for 30 minutes, the nickel nanowires will retain their linear structure. This implies that there exist strong magnetic interactions or other interactions among the particles [22]. The selected-area electron diffraction (SAED) pattern (see Fig. 2b) carried on an individual nickel nanowire consists of diffraction rings, indicating that the nickel nanowires have a poly-crystalline structure.

Figure 3 shows the XRD pattern of nickel nanowires. The diffraction peaks of (111), (200) and (220) are consistent with standard diffraction data of nickel (No. JCPDS 04-0850). This indicates that the Ni nanowires are having fcc crystal structure. No other peaks were observed, implying that the nanowires prepared by this method have high purity and they are not oxidized. The lack of oxidation can be attributed to the fact that nitrogen gas was generated during the reaction process. This phenomenon was also observed and discussed by other researchers [18].

Since external magnetic fields played a very important role in formation of 1-D magnetic Ni nanowires [19,21], we investigated the products prepared without applying magnetic fields. Figure 4 shows the SEM images of the products at 50°C for 30 min without magnetic field. One can notice that the products are nanoparticles and without any 1-D nanomaterials present (see Fig. 4a). From the magnified image shown in Fig. 4b, the size of the particles can be estimated to have a diameter of 100 nm. Therefore, it can be concluded that magnetic field is the prerequisite and mandatory condition to be present in order to grow the magnetic nanowires in this synthetic approach.

In order to illustrate the detailed growth mechanism of the nanowires and the role of magnetic field on the formation of the nanowires, we investigated three samples which were collected during the reaction process. Three samples were collected after the reaction took place for 10 min, 20 min and 30 min. Figure 5 shows that their SEM images and the corresponding schematic illustration of the growth processes of nickel nanowires. One can see at the beginning of the reaction, that is, during the first 10 min the products are mainly particles with diameter of 100 nm, even if the magnetic field of 0.5 T was applied. However, in the second 10 min the particles have been aligned along the magnetic field but the morphology of particles are clear and obvious. After 30 min, the reaction was completed and nanowires with smooth surface were formed. The possible reaction and growth mechanism may be interpreted as follows:
During the first 10 min, hydrazine hydrate coordinates with Ni\textsuperscript{2+} to form a very stable complex Ni(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2}, and this would avoid the formation of Ni(OH)\textsubscript{2} as NaOH was introduced into the solution. The formation of Ni(NH\textsubscript{3})\textsubscript{6}Cl\textsubscript{2} can greatly decrease the concentration of Ni\textsuperscript{2+} in the solution and thus can reduce the reaction rate. This will improve the oriented growth of the nickel nuclei and form spherical particles [23]. In the second 10 min, the magnetic particles were subjected to magnetization in the magnetic field and aligned linearly by the magnetic force. The strong magnetic dipole interactions between magnetic particles will make them align tightly and rapidly, forming the magnetic particle-chains. At the same time, the formation of the chains would enhance the local magnetic field [24]. In the third 10 min, new nickel nuclei deposited near the chains as influenced by strong local magnetic field to form linear nanowires as show in Fig. 5c. The magnetic dipole interactions among the particles are so strong, it is difficult to destroy or break down the linear or chain-like structures even as they were subjected to an ultrasonic treatment for 2h. It must be noted that magnetic dipole interactions among magnetic particles can strongly affect the shape of the nanowires [25].

FIG. 5. Schematic illustration of growth mechanism and SEM images of Ni nanowires taken at three steps during the reaction process: (I) after the first 10 min; (II) after the second 10 min; and (III) after the third 10 min. The scale bars in all the insets represent 200 nm.
Conclusions

In summary, nickel nanowires with aspect ratio up to 300 have been successfully prepared by a hydrazine hydrate reduction method, under applied magnetic field. Nickel ions were reduced by the hydrazine hydrate instead of ethanol. The reaction efficiency depends on the pH value and reaction temperature. A growth mechanism for nanowires is proposed, after investigating the product at three different stages during the synthetic process. The external magnetic field is the key element in the formation of 1-D magnetic nanomaterials, while the strong magnetic dipole interactions among the nanoparticles make the 1-D structure more stable. This work illustrates a facile synthesis of Ni nanowires having high quality. In addition, this synthetic method can be adopted for the preparation of other 1-D magnetic nanomaterials.

This research was supported by the Hi-Tech Research and Development Program of China (No. 2007AA03Z300), Shanghai-Applied Materials Research and Development fund (No. 07SA10), National Natural Science Foundation of China (No. 50730008), Shanghai Science and Technology Grant (No: 0752nm015, 09ZR1414800, 1052nm05500), National Basic Research Program of China (No. 2006CB300406), and the fund of Defence Key Laboratory of Nano/Micro Fabrication Technology.

Received 29 May 2010; accepted 25 June 2010; published online 15 July 2010

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