Transport properties of molecularly stabilized porous silicon schottky junctions

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Abstract. 1-Dodecyne organic molecules (OMs) were chemically bonded to porous silicon (PS) to constitute Si–PS–OMs–metal (M) junctions. PS, which is highly susceptible to atmospheric contamination, becomes stable upon chemical passivation of its surface atoms. Current–voltage curves were studied to understand the charge transport properties, and these measurements indicate clearly that organic passivation unpins the Fermi-level at the PS–M interface. It was believed earlier that Si–PS is the only important interface that controls charge transport in these junctions. We observe that both PS–M and Si–PS interfaces are equally important in influencing the junction parameters when surface states are passivated. The results are discussed in terms of energy band diagrams of these junctions.

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1. Introduction

Emission of visible light from porous silicon (PS) has attracted a great deal of attention due to its better compatibility with existing silicon-based microelectronics technology [1, 2]. Its nano pillars entangled in a complex structure show many interesting physical and chemical properties which are not exhibited by bulk silicon. Structural, electrical and optical properties of this material have been well-investigated with a view to developing optoelectronic devices [3]. Due to its large surface-to-volume ratio, PS is highly sensitive to its surface conditions and hence has poor stability in optoelectronic devices. However, this property has been explored to grow molecular films of high quality [4, 5], immobilize biomolecules [6, 7] and develop chemical/biological sensors [8]. It is also used as an efficient material to remove potentially toxic metal ions from wastewater [9]. For successful utilization in electronic devices, the kinetic stability of PS has to be improved. To achieve this, all conventional techniques of surface passivation have been applied, but none of these were successful in producing a stable material [3], [10]–[14].

Recent demonstration of grafting organic molecules (OMs) on a material surface appears to be a versatile route for surface passivation [15, 16]. Adsorption of thiols on a gold surface to form a self-assembly of molecules is a well-investigated area of research, wherein molecules bind non-covalently to surface atoms of gold [17]. However, the directional nature of surface atoms of a semiconductor permits covalent bonding of OMs. This would create more stable organic–inorganic interfaces and its further manipulation gives tailor-made chemical surfaces [4, 16]. Their use in the formation of electronics would help to develop molecular electronic devices [18]. The stable bonding of various OMs on Si [19]–[21] and GaAs [22] has been studied in detail, it has been shown that these interfaces are highly stable even under adverse conditions. It is worth mentioning that, even after prolonged exposure to atmosphere, chemically modified Si is completely free from surface oxidation [19]. The same approach is also adopted in stabilizing PS with various OMs and its spectroscopic characterizations reveal that these surfaces are more stable [23, 24]. To the best of our knowledge, there are no reports on electronic charge transport in chemically stabilized PS devices. In this paper, for the first time, we present some studies on the charge transport in Si–PS–OMs–metal (M) junctions.

2. Experimental methods

Single crystals of silicon (boron doped, p-type, 4 Ω-cm resistivity, (100) orientation and one-side mirror polished, supplied by Semiconductor Wafer Inc. Taiwan) were used as the
starting material. Samples were degreased in hot trichloroethylene and then dipped into
diluted hydrofluoric acid (HF) for a few minutes to remove native oxide. Back ohmic contact
was formed on the unpolished surface by evaporating aluminium (Al) under a vacuum of
$1 \times 10^{-6}$ Torr; followed by annealing at 700 °C for a few minutes in similar vacuum to diffuse
Al. PS film was prepared on a piece of silicon ($12 \times 10 \text{ mm}^2$) by anodic polarization in 1 : 1
HF: ethanol solution at a current density of 10 mA cm$^{-2}$ for 45 s. This gives a film of 0.5 \(\mu\)m
thickness, which was repeatedly washed with deionized water to remove acid contamination
and this was the starting material for the rest of our work.

The time interval between preparation of PS and formation of its heterojunctions can
significantly affect the device properties; therefore care has been taken to minimize this time
interval. Chemically unmodified junctions were prepared by immediate evaporation of metal
dots (1.5 mm in diameter) on fresh PS through a shadow mask at $10^{-6}$ Torr. This structure
constitutes Si–PS–M (M = Al, Au) junctions. The chemically modified junctions were prepared
as follows: freshly prepared PS was immediately loaded in a Teflon cell (home-made) under
dry nitrogen and it was left for an hour to remove moisture. Gently 1-dodecyne (25 \(\mu\)l, 98%,
Sigma-Aldrich, as procured) was spread on the PS surface followed by immediate addition of
ethylaluminiumdichloride (25 \(\mu\)l, 1 M in hexane, Sigma-Aldrich, as procured); the latter acts as
a weak Lewis acid to initiate the reaction. The reaction was carried out in the above cell for more
than 2 h under nitrogen. Then, it was repeatedly washed with hexane (AR, Merck) followed by
ethyl alcohol and finally dried in air. Metal dots were immediately evaporated under vacuum
to constitute Si–PS–OMs–M (M = Al, Au) junctions. Buriak et al studied chemical bonding
of 1-dodecyne molecules on a PS surface and showed that this produces a stable material
[23, 24]. In the present work, we adopted the same procedure to stabilize PS. Electrical transport
measurements were carried out using a Keithley constant current source (K220) and a Keithley
DMM (A197) connected to a computer. In all the measurements, the forward bias means that
the bottom contact (Si substrate with Al back) is positive and the top metal dot is negative.

3. Results and discussion

Firstly, unmodified junctions of Si–PS–M were studied to check their stability, and current–
voltage ($I–V$) curves were recorded on Al dots under different conditions. To begin with, the
as prepared junction was recorded at room temperature in air and then in vacuum and these
curves are shown in figure 1(a). In both cases, the curves show a good rectification ratio as
observed in earlier reports [25]. It can be seen that in the forward region, the junction is
quite sensitive to atmospheric conditions; it is more conducting in vacuum than in air and corresponding voltages at a current of 1 mA are 5 and 6.7 V. However, in the reverse region,
there is no observable change between the two curves. It appears that adsorption of atmospheric
molecules on the PS surface depletes its majority carriers, which leads to a decrease in electrical
conductivity of the junction. Subsequently, the junction was annealed at 387 K for 2 h in vacuum
and was cooled to room temperature without breaking the initial vacuum. Immediately $I–V$
curves were recorded in vacuum and then in air after exposure to atmosphere for more than
an hour. These results are shown in figure 1(b); when compared with figure 1(a), there are
remarkable differences between the curves: (i) the annealed junction is more conducting in air
than in vacuum, which is opposite to what is observed in the case of the as prepared junction;
(ii) annealing shifts both the curves to the higher side of voltage; and (iii) after annealing, the
curves in the reverse region become sensitive to atmospheric conditions. To test time-dependent
stability, this junction was exposed to air for more than 15 h and then once again curves were recorded in air and in vacuum, as shown in figure 1(c). It is seen that in the forward region, the behavior is similar to the as prepared junction, less conducting in air than in vacuum, but in the reverse region they are different. Similar results are observed in the case of the Si–PS–Au junction, which are not shown in the figure.

These measurements clearly indicate that unmodified PS junctions are highly unstable under atmospheric conditions. The high reactivity of PS with air molecules is not a new phenomenon. It has been reported that even after a year of preparation it reacts vigorously with water, alcohol and toluene by releasing hydrogen gas [26]. In the process it is partially converted to compounds of Si; this high reactivity is attributed to the presence of a large density of surface dangling bonds [3]. The strong intimacy towards adsorbed molecules is also observed in photoluminescence measurements, it quenches when PS is exposed to certain organic vapors [27, 28]. Therefore, it is expected that the partial conversion of PS surface to its compounds significantly affects charge transport properties. It is rather difficult to understand transport properties without knowledge of the chemical compounds that occur on the surface.

Next, we attached 1-dodecyne molecules to the PS surface to understand the stability of Si–PS–OMs–M junctions. Recently, it has been shown that organic passivation of PS gives highly stable surfaces [23], [29]–[32]. As in the case of unmodified junctions, here also one of

Figure 1. Room temperature $I–V$ curves of unmodified Al-junction (Si–PS–M) measured in air and vacuum: (a) as prepared, (b) after annealing at 387 K for 2 h and (c) then exposing to air for more than 15 h.

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the junctions was probed under different conditions. Current–voltage curves of as prepared Al-dots recorded in vacuum and in air are shown in figure 2(a). There is hardly any difference between these curves indicating that molecular passivation of PS is very effective in neutralizing the surface states. The junction was then annealed at 387 K for two hours in vacuum and was maintained at room temperature without breaking the initial vacuum. Once again the current–voltage curves were recorded under different conditions, first in vacuum and then in air after sufficient exposure to atmosphere, these curves are shown in figure 2(b). Curves were further recorded by switching between air and vacuum and there was no observable change, one of these curves is also plotted in the figure. All curves recorded in air and vacuum are identical and exactly reproducible. On comparison of figures 2(a) and (b), it is clear that annealing improves the junction conductivity, the forward voltage is lowered almost by 1.4 V for 1 mA. Similar results are noted in the case of chemically modified Au-junctions (not shown in the figure). By considering thermionic emission as the process of charge transport in these junctions, the diode ideality factor \((n = (e/k_BT)(\partial V/\partial I))\) was estimated to be \(n^{\text{Al}} = 7–8\) and \(n^{\text{Au}} = 29\), which is reasonably high compared to Si–M Schottky junctions. A wide variation in \(n\) (ranging from 3 to 100) is commonly reported for PS–M junctions and is found to be a strong function of doping density and preparation conditions [33]. The large value of \(n\) in our molecularly modified junctions indicates that thermionic emission is not a dominant mechanism of charge transport.

Current–voltage curves were recorded in vacuum as a function of temperature for chemically modified Al- and Au-junctions, measured curves are given in figures 3(a) and (b), respectively. The curves for the Al-junction are almost independent of temperature and those for the Au-junction show a weak dependence. In the latter case, there is a progressive increase in reverse current with increasing temperature. As in the case of the diode, the dependence of reverse saturated current on temperature was used to calculate the energy gap of the semiconductor. It is 0.35 eV, too small to account for the energy gap of either Si or PS. Similar values have been reported earlier and shown to be strongly dependent on the degree of porosity [34]. The most important observation in our measurements is that chemically modified junctions

![Figure 2](http://www.njp.org/)
show metal dependent current–voltage curves (figures 3(a) and (b)), a behavior rarely observed in earlier reports on unmodified PS junctions with various metals contacts such as Pd, Al, Pt, Au, Sb and Ag [35, 36]. This clearly implies that passivation of PS by OMs unpins the surface Fermi-level when it is in contact with metal. This is possible only if the density of surface states decreases upon surface passivation. In many of the earlier reports, it was believed that in Si–PS–M junctions the PS–M interface is not sensitive to the contacting metal and hence is not important in deciding junction parameters [25, 37].

An energy band diagram was constructed for Si–PS–OMs–M junctions of Al and Au by taking their typical energy parameters. PS is a complex material made up of nano wires of silicon (in the range 3–10 nm) having large density of surface states [33]. In the past, an average band gap of 2 eV with equilibrium Fermi-level close to the intrinsic value have been acceptable parameters for many calculations [3]. Experimentally the observed band offsets between Si and PS are \( \Delta E_C = 0.29 \) eV and \( \Delta E_V = 0.59 \) eV [25]. We believe that chemical bonding of 1-dodecyne molecules drastically reduces surface states of PS and creates an ultra thin layer (a few angstrom thick) of molecular insulator having HUMO–LUMO gap in the range of 9 eV, this being an acceptable value for many OMs [38]. With these and work functions of Si and contacting metals the energy band diagram for non-intimate contacts was drawn and is shown in

**Figure 3.** Temperature dependent \( I–V \) curves of chemically modified annealed junctions: (a) for aluminium and (b) for gold; (c) energy band diagram of Si–PS–OMs–M junctions for aluminium and gold contacts under the non-intimate contacts, here the numerical values are in terms of electron volts. \( E_F^{Al} \), \( E_F^{Au} \), \( E_F^{PS} \) and \( E_F^{Si} \) are Fermi levels of aluminium, gold, PS and Si, respectively.
Figure 4. The modified Fowler-Nordheim plots ($\ln(I)$ versus $1/V$) for chemically modified junctions under forward and reverse biases for: (a) aluminium and (b) gold.

figure 3(c). Fermi-levels of both Al and Au are put in the same diagram. Due to the presence of a thin molecular layer between the metal and PS, the charge transport mainly occurs by tunneling of charge carriers. It can be seen that in the Al-junction under a small forward bias metal electrons directly face the conduction band of PS and can tunnel through the barrier and this probability increases rapidly with increasing voltage. Under reverse bias, holes from the metal can tunnel into the valence band of PS, but this probability is very low due to greater separation between the two levels. It is to be noted that the pure tunnel current, in general, is independent of temperature and the Al-junction exhibits this behavior (figure 3(a)). The situation is different in the Au-junction, here the metal Fermi-level is rather close to the valence band of PS and hence in forward bias metal electrons face a higher barrier to tunnel into the conduction band of PS. Therefore, compared to Al-junctions, here tunneling should occur at higher voltages. Under reverse bias, the situation is opposite to that of the Al-junction, the tunneling barrier for holes from metal to PS is relatively low and hence more reverse current can be observed. Therefore, in these junctions it can be concluded that Al acts as a better electron injector (minority carrier device) and Au as a better hole injector (majority carrier device).

In the Fowler–Nordheim (FN) tunneling theory current density is given by [39]

$$ J_{FN} = A E^2 \exp \left( -\frac{B}{E} \right), \quad (1) $$

where $B = (4(2m^*)^{1/2}E_g^{3/2})/(3\hbar e)$, ‘$E$’ is electric field, ‘$m^*$’ is effective mass, ‘$E_g$’ HUMO–LUMO gap of molecular layer, ‘$\hbar$’ is Planck’s constant, ‘$e$’ the electronic charge and ‘$A$’ is a constant. For image force and hot electron corrections the above equation reduces to [39]–[41]

$$ J_{FN} = A’ \exp \left( -\frac{B}{E} \right), \quad (2) $$

where ‘$A’ is a new constant. Equation (2) is used to analyze our data, plots of $\ln(I)$ as a function of $1/V$ for Al- and Au-junctions are shown in figures 4(a) and (b). As per the energy band diagram, at a given forward voltage the tunneling probability is greater in the Al-junction than in the Au-junction which is clearly observed in figure 4(a). The tunneling plots in the reverse
region are also shown as insets in the above figures, the Au-junction displays a better tunneling component than the Al-junction. A small temperature dependent current in the former could be due to defect assisted tunneling which weakly depends on temperature. Its origin in the junction is yet to be understood. Electrical conductivity of Si–PS–M junctions has been reported earlier by many authors; band conduction [36], activated hopping in tails and deep states [37, 42], Pool–Frankel effect [43], inter-crystallite hopping, Schottky emission and FN tunneling [44] were some of the mechanisms that were proposed. But none of these junctions had stable PS and hence it was difficult to accept any of the proposed paths of charge transport. However, good stability of the present junctions due to molecular passivation suggests that tunneling is the main mechanism of charge transport.

4. Conclusions

Surface passivation of PS was carried out at room temperature by covalent attachment of 1-dodecyne molecules. To understand the electronic charge transport, both as prepared and chemically modified PS was used to form Si–PS–M (M = Al and Au) junctions. $I–V$ curves were studied under different conditions and it is observed that chemically modified junctions are more stable as compared to unmodified junctions. Chemical passivation reduces the density of surface states on PS, as a result the interface between PS and metal becomes sensitive to the work function of the contacting metal. The observed results are explained in terms of energy band diagrams for these junctions.

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