Structured nanocarbon on various metal foils by microwave plasma enhanced chemical vapor deposition

G Rius and M Yoshimura
Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, 468-8511, Nagoya, Japan
E-mail: rius@toyota-ti.ac.jp, yoshi@toyota-ti.ac.jp

Abstract. We present a versatile process for the engineering of nanostructures made of crystalline carbon on metal foils. The single step process by microwave plasma-enhance chemical vapor deposition is demonstrated for various substrate materials, such as Ni or Cu. Either carbon nanotubes (CNT) or carbon nanowalls (CNW) are obtained under same growth conditions and without the need of additional catalyst. The use of spacer and insulator implies a certain control over the kind of allotropes that are obtained. High density and large surface area are morphological characteristics of the thus obtained C products. The possibility of application on many metals, and in the alloy composition, on as-delivered commercially available foils indicates that this strategy can be adapted to a bunch of specific applications, while the production of C nanostructures is of remarkable simplicity.

1. Introduction

The potential applications of nanostructured materials can play a major role for the ultimate performance of devices. A particular attention is being paid to the nanosized crystalline C materials. Beyond their use as building blocks for fundamental investigations, they show promise for many applications. There is an intense interest to exploit their electro-optical, mechanical, chemical properties resulting from some specific morphological and structural characteristics. Functional devices made with nanostructured C, such as batteries, supercapacitors, field emission devices, etc. show promise to fulfill the present requirements of charge storage and energy conversion, specially, in terms of efficiency. In other words, they are expected to have capabilities, for instance, to supply both enough energy and power densities for practical operations. Many demonstrators for the proof of concept can be found in the literature, as examples of their advantageous performance. In 2007, Kaempgen et al. [1] demonstrated the supercapacitor performance of CNT electrodes thanks to the creation of superior electrical double layer capacitance. In this case, network of CNTs were deposited onto the metal contacts from solution. More recently, ac line filtering by graphene sheets based on the double layer has also been presented. [2] In this case, the production of C material is based on a growth process similar to the one shown in the present paper. Other strategies for advanced capabilities include nanoparticle-carbon compound materials able to catalyze reactions, such as in water splitting or fuel cells.

Limitations on nanosized C material synthesis include the high control over the crystallinity, purity, and so on. Understanding the process conditions and mechanisms that lead to the different morphologies is essential for their vast consolidation as functional materials. Yet, for transferring such devices from the lab to the market, technological developments for batch fabrication and inexpensive and compatible processing methods are needed. In this communication, we present our findings for the
direct synthesis of carbon nanotubes (CNT) [3] and carbon nanowalls (CNW) [4] on metal substrates. This method allows obtaining high density and large surface area C material in a single process and upon conductive supports, which is ideal for charge storage devices. It is produced by microwave plasma enhanced chemical vapor deposition (MPECVD) on as-purchased metal foils.

2. Experimental

We employ a commercial apparatus, CVD-CN-100 from Ulvac Japan Ltd., similar to the setup used in [4]. The synthesis conditions are common for all the different substrates presented herein. Whole process is realized at a constant pressure of 1.5 Torr and assisted by microwave field of 2.45 GHz and 500 W. In particular, nanocarbon material synthesis consists of two steps. First, surface conditioning by H₂ flow during 3 minutes and applying an electrode bias of 100 V; followed by 10 minutes C deposition. The C precursor is CH₄ mixed with H₂ in a 1:1 ratio (20:20 sscm) and 200 V bias for the generation of plasma. The preliminary stage under H₂ flux has a double function; it cleans and prepares the metal for C deposition, but also preheats the chamber and sample. There are no sample stage or chamber tube heaters, so temperature increase is driven by microwave absorption and resulting energy transfer in the plasma environment. Our group has been studying the conditions of synthesis for the CNWs as a function of feedstock gases. [5] Based on that investigation, we test and analyse here the possibility of diversifying the substrates for specific applications (the metal foils) and their effect on the C nanostructures deposition.

As for the substrates, we use commercially available metal foils of high purity by Nilaco (Ni, Cu, constantan, Mo, Ti, etc.). For convenience, we center the presentation of the experimental results and discussion only to metal foils containing Ni and Cu. The choice of Ni and Cu is rooted on the fact that they are the most commonly used catalysts for graphene deposition. Specifically, we show the products obtained on Cu foil of 500 μm thickness, Ni foil 300 μm and Ni-Cu alloy containing 45 % Ni and 55% Cu (namely constantan) of a thickness of 500 μm. SiO₂ on Si chips are also used, either as deposition sites or for isolating the metal foils from the sample stage (underneath the metal foil and onto the Mo sample stage, lower electrode). As insulator and spacer, alumina crucible is employed as well. The necessity and function of the electrical and spatial isolation are presented in the description of results and discussion for the experimental products. Typical sample size is smaller than 1 cm².

![Figure 1. Top view SEM images of nanostructured C deposited on the metal foil using 100 nm thick SiO₂ on Si as the stage-metal separator. a) CNWs are obtained on the Cu foil. b) For Ni foil, CNTs are grown without the addition of catalyst particles to promote the CNT nucleation sites.](image)

Characterization is here based on scanning electron microscopy (SEM) and Raman spectroscopy for the observation of deposited C morphology, arrangement, density, etc. and the structural identification of nanocarbon products, respectively. Optical observation is applied to the determination of extension and uniformity of C deposition coverage. SEM instrument is a field emission Hitachi
S4700, operated at 20 kV, and Raman spectroscopy is done with an inVia Reflex from Renishaw, using a 532 nm excitation laser, ~0.3 mW, 10 s accumulation times.

3. Results and discussion
Two major parameters have been investigated as deterministic conditions for C nanostructuring on various metal foils by MPECVD, i) the substrate material, [6] and ii) the effect of local distribution or configuration of electric field during C deposition. [7] Depending on substrate material, changes of C solubility in metal, absorption of microwave field (leading to local temperature increase), and creation of particles to promote CNT formation, deposition sites for CNWs, etc. are reported to determine C deposition. [8] The influence of field and plasma distribution can also be found in the literature. [9, 10]

We present the potential and strength of our approach as follows.

Figure 1 shows the results of C deposition onto samples of Cu and Ni foils. Different from other supports that will be introduced later on (see Figure 2), metal foil pieces were placed on top of a 100 nm SiO$_2$ on Si chip during MPECVD process. This way, we isolate physically the metal foil from the stage to have a reference with bare SiO$_2$ substrate as C deposition site [5] to evaluate the metal role and to prevent stage contamination. On Cu foil, packed randomly-oriented CNWs are formed (Figure 1, a)). The vertically arranged graphene flakes are less than 2 $\mu$m in height, and ~200 nm to 1 $\mu$m across. On the other hand, vertically aligned multiwalled CNTs (MWCNTs) of diameters ranging from ~15 to 60 nm are produced onto the Ni foil (Figure 1, b)). It is worth remarking this point. CNTs are produced without using specific or additional catalytic particles and that CNT formation does not occur for Cu foil under same processing conditions. These two facts suggest that the tubular growth is possible in the case of Ni due to the solubility of C. The CNT formation may proceed by C nucleation and diffusion [6] in the protrusions formed on the Ni surface due to plasma bombardment and heating, probably, stretching metal from the foil to form catalytic particle.

Figure 2. CNWs deposited on Cu using a) 500 nm SiO$_2$ on Si and b) alumina plate, underneath the metal foil. c) CNTs and d) CNWs grown on Ni using 500 nm SiO$_2$ on Si and alumina plate, respectively, underneath the metal foil.
The deposition of CNWs in a Cu foil presents a higher density as compared to the bare SiO$_2$ substrate (data not shown [11]). This can be attributed to the metal through an increase of catalytic activity and, probably, effective temperature. The low solubility of C in Cu promotes the C species to accumulate on the surface and prevents the CNT formation, but the state of the substrate after H$_2$ flow conditioning can affect as well. Atomic force microscopy imaging [11] demonstrates that pre-growth H$_2$ treatment smoothes the Cu foil at the micron scale, but causes tiny protuberances in the nanoscale range at the same time. These Cu nanograins on the same Cu foil perhaps additionally promote the vertical arrangement of the multilayer graphene sheets when assuming the Volmer-Weber growth mechanism [2] consisting in horizontal C nucleation islands that become perpendicularly arranged to the substrate by mutual impingement during growth.

The fact that C deposition does not occur on Si samples placed in contact with the Mo electrode (sample stage), but it does in SiO$_2$ motivated the analysis of spacer effect. The results are exemplified and summarized in Figure 2. In the case of Cu foil pieces, we obtain always similar results using SiO$_2$ on Si of 100 nm (Figure 1, a)) and 500 nm SiO$_2$ thickness (Figure 2, a)) or the alumina crucible (Figure 2, b)), a high density of CNWs. However, for Ni foils, lower amount of CNTs are produced if spacer of 500 nm SiO$_2$ on Si is used (Figure 2, c)) (to be compared to Figure 1, b) for 100 nm SiO$_2$ on Si) and CNWs are obtained when using the alumina crucible (Figure 2, d)). We understand this phenomenon as a demonstration of the importance of the plasma distribution and related electric field for the conditions that lead to C deposition and structuring. [9, 10]

![Figure 3](image-url)

**Figure 3.** a) Raman spectrum of CNTs deposited on a Ni foil. b) Tilted SEM image of CNTs* grown on constantan foil.

An example of structural C nanomaterial characterization is shown in Figure 3, a), in particular, for the CNTs deposited on Ni foil. Raman spectra present the typical D-band, G-band and 2D-band Raman signatures of graphene-like material at $\sim$1350 cm$^{-1}$, $\sim$1590 cm$^{-1}$, and $\sim$2695 cm$^{-1}$, respectively (similar would obtained for CNWs). The ratio and FWHM of G to 2D peaks confirm the multilayered structure of both CNWs and CNTs. [12] The high D peak accounts as well for the multilayered CNTs and the defects and imperfections of CNWs, high density of edges [13]. In addition, a small shoulder in the G-band is observed at 1620 cm$^{-1}$ and is assigned to the D’-band, which also relates to disorder. [14] The common Raman features of CNTs and CNWs limit further analysis of materials, but could quantify and discern the presence of graphitic C or solid C fibres, if abundant. In this sense, Raman spectroscopy may not be informative of hybrid structures such as the all-C flake-decorated CNTs, named as CNTs*, shown in Figure 3, b). These kinds of materials are extremely attractive due to their intrinsic larger surface area or field emission properties. [15] Actually, the fact that micro-Raman characterization averages data from microns wide area does not allow to obtain individual CNT or CNW information in order to formulate more precise structural statements, such as the number of layers or inner structure of CNTs. Transmission electron microscopy would be
ideal, especially to observe the resulting CNT catalyst particle size and shape. However, this analysis goes beyond the scope of present communication and no pristine representative data would be easily obtained.

The CNTs* can be easily obtained when using Constantan foil pieces (Figure 4), likewise processed as on Ni or Cu foils. Again, the use of SiO$_2$ on Si spacer makes possible the C structuring in the form of CNTs (Figure 4, a and b)), while CNWs are deposited if using the alumina crucible as separator (Figure 4, c)). More uniform diameter of the CNTs (Figure 4, a)) is obtained, which indicates that certain particle aggregation is prevented by metal alloying. In the basis of Ni versus Cu results, where CNT were only grown upon Ni and lower density (Figure 4, a) in opposition to Figure 1, b)), the use of Ni-Cu alloy reinforces the idea of the need of C solubility inside the metal to form CNTs in present MPECVD conditions. Furthermore, the use of Constantan combined with 500 nm SiO$_2$ on Si spacer, in Figure 4, b), generates amount of CNTs*, that is the flake decorated together with protruded CNTs, which may be related to the presence of Cu in the form of particles. Other alloys, such as so-called Advance (Ni-Cu-Mn), lead to similar structuring mechanism and stressed the material selectivity, and consequential, density dependence as well. The possibilities of directly tuning the C nanostructuring, using combination of many materials and adjusting of synthesis process are of application-oriented significance.

![Figure 4](image)

Figure 4. Nanostructured C materials produced on Ni-Cu alloy as a function of the mediator between metal sample and sample stage, a) CNTs, by 100 nm SiO$_2$ on Si, b) CNTs*, by 500 nm SiO$_2$ on Si, and c) CNWs, by alumina crucible.

Final remarks related to the present development are included to highlight the importance of the spacer. In addition to what has already been demonstrated, we observe a drastic change in nanocarbon catalysis and its arrangement if spacer is not used. For instance upon Cu foils, whereas electric isolation with respect to sample stage promotes the vertical arrangement of C nanostructures (the CNWs), metal foil making contact with Mo electrode leads to the layered deposition of some amount of low graphitized carbon, horizontally covering the Cu piece. This behavior suggests that physical and electrical contacts are deterministic and intrinsically related for the plasma conditions used in this synthesis processing conditions. The same MPECVD system is being used in another of our technological approaches to integrate CNTs into atomic force microscopy probes. In this application, we use the vertically aligned multiwalled CNTs to functionalize only the vicinity of the tip apex of commercial Si probes. [16] In this application, it is also primordial to introduce some sort of discontinuity that compensates the tip morphology effect. We use a homemade sample holder with membranes to screen the electric fields and ion species during growth, in such a way that their deceleration permits the CNT growth. A dedicated study to analyze this effect in base of CNW growth in Cu foils has been realized and will be soon released for publication. [11]
4. Conclusions
In summary, we have presented a versatile process for the engineering of nanostructures made of crystalline carbon on metal foils. The single step process has been applied to various materials to obtain CNTs, CNTs* and CNWs under same growth conditions and without the need of additional catalyst particles. The use of insulator and spacer implies a certain control over the kind of allotropes that are obtained. High density and large surface area are morphological characteristics of the products.

Present strategy to tune the morphology of deposited C nanostructures by processing configuration and elements is an alternative procedure to the C nanoengineering by feedstock gases and use of nanoparticles. The properties of CNWs on Cu foils as electrochemical double layer capacitor are being tested and show an excellent performance for supercapacitor application. The possibility to be applied to other metals and on as-delivered commercial samples indicates that this strategy could be adapted to many specific device requirements. For example, it could be exploited for a bunch of materials (compound contents, e.g. alloys) or to adjust C nanostructures density or inorganic functionalization, at the same time as the production is of remarkable simplicity and controllability.

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