Synthesis Control for Carbon Nanowalls on Copper Supports for Development of Green Energy Applications

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We present the phenomenological study of process parameters, characteristics and limitations of carbon nanowalls (CNW) growth by means of microwave plasma enhanced chemical vapor deposition in order to optimize the synthesis of CNW samples for targeted applications, such as supercapacitors or batteries. The growth of CNWs directly onto commercial Cu foils is simple, resulting in a higher density as compared to SiO$_2$ or alumina supports. Complete chip coverage by CNW deposition is restricted to $\sim 1$ cm$^2$ squared Cu foil pieces. This is due to some electric field distortion by the use of insulating spacer and certain microwave field contribution. As a result, anisotropy and localized distribution of plasma species and conditions that enable the CNW growth is promoted. Testing the charge storage capability of our CNWs on Cu foil evidenced the suitability of present synthetic approach for the development of supercapacitor devices. [DOI: 10.1380/ejssnt.2012.305]

Keywords: Carbon nanowalls; Plasma processing; Nano-films, stacks, and other nano materials; Nano structure chemistry, processing and fabrication

I. INTRODUCTION

Carbon nanomaterials are in the spotlight of the research community and the industry. While carbon nanotubes (CNT) can provide superior performance, for example, as a part of composites [1] or for scanning probe microscopy applications [2], fullerenes show promise for medical applications [3] and more recently attracted the attention for their use in solar cells [4]. In the case of graphene and graphene-based materials the list of applications appears to be unlimited, including almost any field, electronics, optics, chemical sensors, etc [5].

Their potential and impact derive from the exceptional charge transport, thermal, optical and mechanical properties, which are determined by their specific structure and dimensions. Those characteristics could be tailored, in particular, for solving the present increasing and intensive energy demands. The use of nanostructured carbon materials as supercapacitor material [6] or field emission devices [7] is demonstrating an outstanding performance, as well as, becoming interesting substrates for catalysis, energy conversion or material storage [8]. For these applications, large surface area, sharp edges, electrical conduction, etc are required. All these characteristics are fulfilled by the graphene sheets and the vertically arranged multilayer graphene, namely carbon nanowalls (CNW) [9].

We present the study of process parameters, characteristics and limitations of CNWs growth by means of microwave plasma enhanced chemical vapor deposition (MPECVD), from a technological point of view. The goal of the investigation is to optimize the CNW synthesis products for targeted applications, such as supercapacitors or batteries. The growth of CNWs onto metal supports, such as the herein presented commercial copper foils, is additionally simple and, therefore, advantageous [10]. Deposition results in a higher density as compared for example to SiO$_2$ or alumina supports. The area-limited distribution of the deposition among the Cu sample is apparent and strongly affected as a function of chip size, shape and so on. While understanding the origins of such anisotropy, the study of the areal dependence allows to us to determine the proper chip dimensions for a complete and uniform coverage of the Cu substrate with high density of CNWs over a reasonable region which enable real applications. Testing the charge storage capability of our CNWs on Cu foil evidenced the suitability of present approach for the development of supercapacitor devices [11].

II. EXPERIMENTAL

The deposition of the CNWs is done onto as-purchased pieces of Cu foils, with no preliminary treatment or preparation. These polycrystalline foils are commercialized by Nilaco, of guaranteed high purity (99.9%) and 500 $\mu$m thick. Sample size varies in the order of 0.5-2 cm (for length and width). During processing they are placed on top of an alumina plate piece, as it will be described in the next section and discussed previously in [10].

The MPECVD system is a CVD-CN-100, from Ulvac Japan Ltd., designed for CNT deposition [12]. It is equipped with a microwave power supply, 2.45 GHz and 500 W, coupled with a rectangular waveguide perpendicular to the cylindrical glass chamber where the samples are processed. The microwave source is located 111 mm from the center of the electrode plates and plunger to reflect the microwaves is adjusted 75 mm (3/4A) apart in the opposite side. The glass cylinder is 51 mm in diameter and 240 mm in length. DC bias is applied by two parallel circular Mo plates, separated 42.5 cm in the longitudinal direction inside the glass chamber and 4 cm in diameter. Lower position electrode (cathode) is used as the sample stage. Gas supply is introduced from the upper part of the glass tube and pumped out by the lower part, so that feedstock flow conditions at the sample processing space are steady.
The growth of CNWs consists of two stages. First, 20 sccm H$_2$ gas feed is flown during 3 minutes, while raising the DC bias from 0 V to −100 V. Then, the carbon deposition is done with a gas mixture of CH$_4$:H$_2$ flow rate of 40:40 sccm during 10 minutes. This part includes a 2 minutes period to raise DC bias from −100 V to −200 V, reaching a steady current of ~230 mA. All the process is kept at a total pressure of 200 Pa (1.5 torr) and with the microwave field being on.

Products of MPECVD are observed optically and using a scanning electron microscope (SEM). Macroscopic determination of the extension of the foil chip covered by CNWs is recorded with a digital photo camera and confirmed by SEM inspection. The morphology and density of the CNWs is revealed in a field emission SEM Hitachi, S4700 operated at 10 kV.

Morphological characterization is assisted occasionally with Raman spectroscopy, 532 nm wavelength [13]. The CNWs consist of a structure very similar to that of the graphite, so that their Raman signature is close as well. Typically, the spectra are characterized by the height of the peak at the D-band (~1353 cm$^{-1}$), which is disorder-induced active mode and accounts for the high density of edge states [14]. Atomic force microscopy (AFM) has been used to evaluate the condition of the surface after the H$_2$ portion of CNW deposition processing. Scanning probe microscope system is a Seiko Instruments NanoNavi II E-Sweep and Si cantilevers with Al reflection coating are used in the non contact dynamic mode of AFM operation (Budget Sensors Inc. Model: TAP300AL, 300±100 kHz, 40 N/m).

III. RESULTS AND DISCUSSIONS

Different from the CNTs which are produced generally in base of nanosized metal particles to favor the tubular nanostructuring, CNWs do not require such morphological catalysis [15]. Figure 1 shows the CNWs synthesized by MPECVD on an alumina plate piece (left) and a Cu foil sample processed onto alumina piece (right). Our group has also reported the possibility to grow CNWs on SiO$_2$ supports [10, 16], which indicates that deposition is not essentially restricted by the material. Those results also showed an elevated growth rate in high, superior than other cases in the literature [17] which can vary even in a few orders of magnitude, and how it correlates to the precursor amount.

While dense CNW deposition is achieved on both supports, it has been noticeably more efficient in the Cu sample, systematically. This is not exclusive from Cu, but has been also observed for Ni foil pieces subjected to similar processing conditions [10]. One should note that the only difference between substrates in Fig. 1 during the growth, the alumina (left) and Cu (right), is the addition of the metallic piece (Cu) onto the alumina. Additionally, present results demonstrate that initial surface roughness is not very relevant, Cu foil and alumina plate are quite uneven especially if compared to SiO$_2$.

Traditionally, the sample size for the CNW growth tests has been 5×5 mm$^2$ (about 0.5% of the electrode area), so that uniformity of the plasma on the chip is guaranteed and placed at the edge of the electrode that is closer to
FIG. 4: Simplified sketches representing the space distribution, power flux of the electromagnetic fields and causes of the local and particular distribution of plasma species. (Left) Without the insulator/spacer to separate the Cu foil from the substrate, plasma ions are too energetic to permit the nanostructuring of C, whereas alumina plate promotes charging that possibly will screen and slow down the energetic charged species making possible the CNW deposition. (Center) Metal placed upon insulator during process lead to the noticeable anisotropy in the CNW deposition depending on the sample configuration and size. (Right) Microwave field and electric field is concentrated in the front wave part when sample size exceeds about 1 cm in width, so that the plasma conditions for deposition become restricted within the chip in depth.

FIG. 5: Complete sample area coverage has been achieved on circular samples (radius 1.2 cm), as seen here, and quasi-squared (1×1.2 cm²). This particular pair of chips has been tested for the supercapacitor application in a three electrodes configuration, evidencing the CNWs capability for the formation of the electrochemical double layer capacitance [11].

the microwave field source. However, motivated by the goal of testing the supercapacitor performance of CNW on Cu foils [11], larger area is requisite to obtain more reliable characterization of the device characteristics.

In consequence, once checked that present processing conditions are suitable for the CNW on the Cu foils, we tested the use of larger Cu pieces. Some exemplary results are shown in Fig. 2, for samples exceeding 1 cm in lateral dimensions. As it can be easily appreciated, the area of the sample covered with the CNWs (black region) is incomplete. In particular, deposition is limited along the microwave direction (expressed here as, in depth, and corresponding to the herein named length of the chip), and inversely to the transversal sample size (called, width of the sample). The total CNW-covered portion of the chip is approximately 100 mm² for all the cases. The area of Cu-like color is covered with some thin amorphous carbon layer, as deduced from Raman signal and optical contrast observation.

This evidence of MPECVD inhomogeneities could be attributed to a certain extent to a predictable plasma distribution as a consequence of the lateral microwave field, which would be located at the electrode plate edge [18] (in particular, Figs. 16 and 17 in p. 17). However, we discarded such statement when executing the CNW deposition with the samples placed at the center of the sample stage.

Figure 3 certainly accounts for the same anisotropic deposition when sample is located in the middle of the electrode plate and for chips with a size similar to the results reported in Fig. 2. The trial avoiding the sharp corners of the sample also confirmed that the concentration of the deposition at incoming microwave front is correlated to chip width size, rather than the pronounced edges of the sample (Fig. 3, right).

To recapitulate the phenomena occurring with the implicated materials, configuration and processing conditions, we schematize the main findings as shown in the three drawings included in Fig. 4. When the process of MPECVD is realized on a conductive substrate in electrical contact with the sample stage-electrode plate [19], no CNW deposition is obtained in present conditions. To illustrate with an image we call it a splash-like process (Fig. 4, left) where C deposition rate and ion species etching might be of the same order, preventing an effective C nanomaterial growth. The sample acts mainly as an extension of the Mo electrode. This behavior could be rooted on the accelerated ion species, that is, low concentration or ultrafast flux on the sample surface avoiding its ordered crystallization.

On the other hand, on an insulating substrate (e.g. SiO₂ or alumina–Fig. 1, left) or isolating the metal sample from the electrode by means of an alumina piece (Fig. 1, right), the target substrate is electrically floating [20], so that a local electric field discontinuity is introduced between the apparatus electrode plates (Fig. 4, left and center). As a result, the gradient of charges within the plasma sheath is locally altered and the true net fields on the sample vicinity will vary. Similarly it will happen for the conditions for the CNW deposition due to bending of the plasma species and effective temperature.
The configuration also implies that insulating sample will experience some charge up. This scenario would stress some distortion of the electric field and, therefore, of the ion species and concentration favorable for the CNW formation [21], but not promoting the complete coverage of the target sample. Specifically, charging can cause a certain screening of the incoming ion species, so that the C incorporation to the surface is enhanced (i.e. growth proceeds), in opposition to the effect on the rate of ion etching events. This is depicted as a sort of sample wrapping effect (Fig. 4, center) that also involves the role of the alumina piece underneath the Cu foil as a spacer, promoting some reflux of C-containing species.

Including now in the illustration the lateral inhomogeneities of the microwave field encountering the suspended sample that exceeds about 1 cm in width, we depict the idea of the confinement of the CNW deposition to the front side of the sample closer to the microwave source, in the Fig. 4, right. Experimentally, the plasma is observed brighter in the microwave incoming side. It also suggests how the in depth incursion is correlated inversely to the width of the sample.

We consider as well the metal presence [18], for a higher CNW deposition density, i.e. boosting of the C nanomaterial formation as it occurs for CNTs or graphene, and probably a certain enhancement of the concentration of the electrical field and plasma species in the microscopic level, coupled to probably a higher effective temperature. The complexity of the plasma-based synthesis is originated in a mix of numerous factors, such as the multiple ionic species, various reactions involved, non-equilibrium phenomena and time dependent state of the materials, e.g. non uniform fields, temperature, pressure at the centimeter, micrometer, nanometer scale, etc. [22].

It was not the aim of this work to provide a precise description of the mechanism of CNW formation and especially of the nanometer scale local events of CNW growth and atom by atom piling up, but a description for the qualitative understanding of the MPECVD variables and the resulting products. More importantly, this study enabled us to determine the suitable size sample dimensions for a complete high density CNW coverage of the Cu foil support, a regular piece of about 1-1.2 cm lateral size. This sample size represents ~2% respect to the total electrode area. To the best of our knowledge, this is the first time that a description on the areal deposition capability for the deposition of CNWs is discussed. On the basis of our findings, we estimate that this is the threshold that the electromagnetic fields, and their interaction with the gas environment, can stand in order not to show a restricted CNW deposition area onto the target sample. Considering this, we hypothesize that for other MPECVD systems this behavior will be similar under equivalent conditions. In particular and to address a general consideration for practical applications of CNWs, scale up of the CNW growth area would require proportional increase of the electromagnetic fields extension and power. Obviously, adjustment of the gas mixture composition and rate (pressure and flux), and processing time for example if lower deposition rate is chosen, might provide some degree of freedom to overcome present limitation and to compensate system differences. An example of the complete coverage of maximized area is shown in Fig. 5 for two circular samples (convenient to perform a robust coin-cell electrochemical characterization).

Similarly, we do not address in this paper a deep discussion on the CNW morphology because we notice that within a single sample we can have small variations, slightly wavy versus straight walls, for example, with no apparent correlation. However, we conclude the analysis with some notes about the local properties of our CNW products and intermediate materials.

In Fig. 6, left, an AFM image of the Cu sample after the H$_2$ treatment stage is included. It can be observed that sample surface is slightly more uniform at the tenth of micron scale, while a closer look evidences the formation of tiny Cu protrusions of nanometer scale size as a result of energetic H chemical species etching. It should be mentioned that this never lead to CNT formation on Cu foils when complete processing is applied [23], which would be a manifestation of the low solubility of C in Cu.

Another particularity can be seen in Fig. 6, center. In this case, we observe the formation of C whiskers growing, roughly, perpendicularly onto the CNWs, which always align in the vertical direction, perpendicular to the substrate, often coincidental to the axis of the DC electric field. This has been attributed to a local reconfiguration of the electric fields [21] and we consider if it could
have some relation with a growth saturation effect due to charging or even consequence of the growing CNW morphology (enhanced electric field due to the CNW built-up or its sharp edges).

Finally, as seen in Fig. 6, right, the directional alignment of CNWs (generally randomly oriented on the sample surface) is apparent at the sample edge of this SiO$_2$ support. We present this instance as another indication of the deterministic effect of strength and anisotropy of the local conditions of the electric field and, consequent, plasma distribution that do contribute to the CNW growth.

IV. CONCLUSIONS

To conclude the present communication, we have introduced a phenomenological description of the CNW growth by MPECVD on Cu foil substrates. First, the experimental results have been presented with the aim to understand the sample parameters involved in the particular CNW deposition distribution. Then, the whole systematic study has been analyzed in order to build qualitative model that explain the growth products taking into account the involved processing conditions.

In particular, the insulating alumina support, acts as a key point to make possible the efficient growth of CNWs. The high rate of CNW growth is attributed to the charging effect and metallic material enhancement of growth, combined with the distortion of the electric field and resulting plasma distribution that causes a localized CNW deposition region on a macroscopic scale. From a practical point of view, the investigation has allowed us to determine the sample size limitations of present processing conditions for a uniform, high density and complete coverage of the Cu piece. This enabled the use of CNWs grown on Cu foils for the development substrates suitable for Green-energy applications, such as supercapacitors devices [11, 24] and batteries [25].

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