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Catalytic growth of carbon nanowires on composite diamond/silicon substrates

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ABSTRACT

Polycrystalline diamond (PCD) films and carbon nanowires (CNWs) provide individually highly attractive properties for science and technology applications. The possibility of carbon composite materials made from a combination of these materials remains a potential approach widely discussed in literature but modestly investigated. We report in this work an early attempt to explore this opportunity in the light of some specific experimental considerations. Carbon nanowires (CNWs) are grown at low temperature without the conventional use of external hydrocarbon vapor source on silicon substrates partially covered by a thin film of coalesced micrometric CVD diamond. Composite substrates constituted by PCD on silicon were first cleaned with H_2 plasma then used for the PVD deposition of 5 nm Ni thin films. Then, samples were heat treated in a CVD reactor at 580 °C in the presence of pure H_2 pressure of 60 hPa at different annealing times. Comparative effect of annealing time on the dewetting of Ni thin films and the subsequent CNWs growth process was considered in this work using systematic observations by SEM. Possible mechanisms underlying CNWs growth in pure H_2 gas were proposed. The nature and structure of these CNWs have been investigated by TEM microscopy and by Raman spectroscopy on the sample showing the highest CNWs density.

1. Introduction

Carbon related materials are subject to extensive efforts over the last years owing to their large potential use and substantial technological applications (solar cells: [1]; energy: [2]; electrical applications: [3]; bio-medicine: [4]). Among these materials, diamond is the most prominent thanks to its superlative properties required for diverse advanced applications [5–8]. The necessity to improve its intrinsic properties and widening its use has first yield to synthetic diamonds [9,10] and therefore to a variety of high quality diamond thin films with various prospects [11–14]. Either structural (bulk) tailoring [15–17] or combination with other materials [18–20] were investigated in order to improve the performances of these reduced structures.

Few studies have envisaged the later issue in a kind of a useful combination. Indeed the combination of PCD thin films with other carbon based materials showing also interesting intrinsic properties provides a prospect to accomplish composite materials of superior performance (CNT/diamond: [18] and graphene/diamond: [21,22]). CNTs are found to be particularly good candidates as they offer the opportunity to confer to the materials in which they are incorporated enhanced performances. For example, growth of CNTs on carbon-based substrates is reported to enhance the mechanical [23,24] or electrochemical [18] properties. Furthermore, this possibility route may provide some clues as to the understanding of the mechanisms that reactions lead to these nanoscale carbon filaments which remain divisive even they are widely studied.

The experimental conditions to synthesize these materials are often different or at least far which growth mechanism of CNWs remains controversial despite the large experimental progress in the field last years [25–28] (and references therein). To the best of our knowledge, only Varanasi et al. [29], Quinton et al. [30], Yang et al. [31] and Hébert et al. [18] have reported the use of CVD diamond film substrates with catalytic metal droplets to grow such filamentary structures. In the two former studies, the authors have carried out CNT growth directly on diamond facets by T-CVD (standard Thermal CVD) or PECVD (Plasma enhanced CVD). In the two later studies, the authors obtained CNTs by using the HFCVD method (Hot Filament CVD). Hébert et al. have developed specific process to obtain CNTs partially embedded in porous diamond films. This CNT embedding induces a strong increase in the CNT/Diamond adhesion and improves the lifetime of the composite electrode [18]. The corresponding growth mechanism reported in these studies is called “base-growth model” where catalytic metal droplets remain anchored on (or in) the diamond films except for Yang et al. where metallic droplets are located on each tip of the

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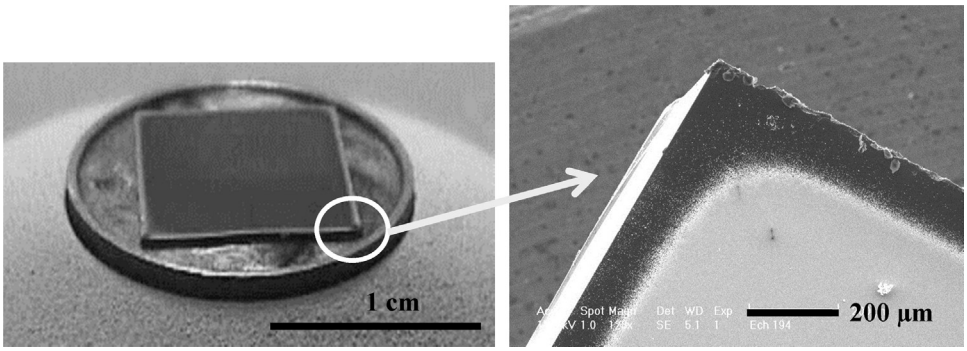

Fig. 1. Left: As grown diamond thin film deposited on silicon substrate. Right: SEM image showing the evolution of diamond crystals density at the edge of the Si substrate.

CNTs (tip-growth model) [31]. In all those works, CH_4 or C_2H_2 have been used as carbon source for CNT growth.

In the present work, we address the objective to grow CNWs on PCD/silicon substrates. We consider the possibility of low temperature catalytic growth of CNWs on diamond thin film by the T-CVD process without the standard use of external hydrocarbon source in the reactive gas. For that, we rely on the ability of the diamond-Ni-gas interactions to directly produce carbonaceous species for CNWs synthesis.

2. Experimental setup

2.1. Diamond/silicon substrate preparation

CVD diamond/silicon substrates were prepared in a modified ASTEX CVD where CVD diamond nucleation on single silicon pristine is obtained by an *in situ* cathodic biasing of the substrate under a high CH_4/H_2 ratio. This technique, so called Bias Enhanced Nucleation (BEN) and described in detail elsewhere [32], allows us to precisely control the nucleation density over the silicon surface by modifying the bias voltage (typically 120 V) and the duration (between 1 min and 5 min in our case). Our samples consist of 1 cm^2 square (0 0 1) silicon wafer on which PCD deposit is grown by microwave plasma chemical vapor deposition technique (MPCVD). The experimental conditions for the growth sequence following the BEN step is chosen to obtain randomly oriented diamond crystals with sizes varying from nanometers to micrometers and exhibiting well defined (0 0 1) and (1 1 1) facets (total pressure 20 hPa, microwave power 300 W, 2 vol.% CH_4 in H_2 at a flow rate of 300 sccm). From these conditions of nucleation and growth, the diamond density decreases from coalesced to isolated crystallites when we move toward the edges from the center of the silicon substrate as shown in Fig. 1. Depending on the surface location, only diamond facets are present on the surface (high nucleation density), or diamond crystallites and silicon (low nucleation density) or only silicon surface (very low or null nucleation density). Thus, we can distinguish three regions depending on the surface location; high diamond nucleation zone where only diamond facets are observed; low diamond nucleation zone where both diamond crystallites and silicon are apparent; and no diamond nucleation zone where only silicon wafer is present. In the following our samples will be also designated as diamond/silicon composites.

2.2. Diamond/silicon plasma cleaning

Before the metallic thin film deposition, the diamond/silicon composite was systematically submitted to hydrogen microwave plasma cleaning in order to reduce surface impurities and contaminants [33]. This step was carried out in the MPCVD reactor at 20 hPa under a 100 sccm pure hydrogen flow during 15 min.

2.3. Metallic thin film deposition

After the plasma cleaning, diamond/silicon composites were immediately placed in a magnetron sputter-deposition chamber equipped with a nickel target. Sputtering deposition rate was previously determined taking into account the synthesis conditions to obtain a thin layer of 5 nm nickel (0.5 Pa under 75 sccm Argon with a Ni target current fixed to 0.2 A during 30 s). The substrate is clamped in front of the nickel target and its temperature was kept at room temperature. More specifications and schematic representations about the experimental sputtering device can be found elsewhere [34].

2.4. Metal dewetting and nanowires growth

Dewetting process of the metallic Ni thin films deposited on the diamond/silicon composite was performed in the MPCVD reactor under pure hydrogen flow. The heating was ensured via an induction heating system located under a molybdenum substrate holder receiving the diamond/silicon composite. Substrate temperature was measured by means of a pyrometer (IRCON).

Prior to the thermal treatment, pure hydrogen was admitted into the chamber and the pressure was stabilized at 60 hPa with a total flow rate fixed at 1000 sccm. Then the inductor is switched on and the temperature progressively increases up to 580 °C in a few minutes. At the end of the heating process, the sample is cooled down at ambient temperature under hydrogen flow. The hydrogen pressure and the heating temperature were chosen according to preliminary tests no reported here.

The crucial difference with other experimental works is that no hydrocarbon species are introduced in the gas phase. Only the diamond crystals are the unique carbon source in our experiments. The heating duration has been adjusted between 15 min and 2 h in order to characterize the different steps from metal dewetting to CNWs growth.

2.5. Characterization

Samples surfaces were morphologically characterized by SEM microscopy using a Field emission gun scanning electron microscope (FEI-SEM; Philips XL30 FEG). Raman spectroscopy (Jobin-Yvon LabramHR with 532 nm excitation laser line, 1800 L/mm grating and CCD detection) was used to determine the nature of the material present after the heating step either on the silicon surface or on the CVD diamond facets. Transmission electron microscopy studies were carried out using Jeol ARM 200F cold FEG associated to EELS spectrometer and GIF Quantum ER to determine the chemical composition and the structure of the synthesized nanowires. The sample was deposited on a holey carbon film 200 mesh copper grid.