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Synthesis of diamond nanocrystals on polyimide film

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ABSTRACT

Sulfur-assisted hot-filament chemical vapor deposition (HFCVD) was recently employed to grow diamond nano-crystals on polyimide film [F. Piazza, G. Morell, Diamond and Related Materials, 16 (2007) 1950], unambiguously showing that the substrate temperature was below 360 °C, the polyimide glass transition temperature. This accomplishment has opened the door to employ diamond in a wide range of applications where it needs to be integrated with temperature sensitive materials. The result reported earlier relies on visible Raman spectroscopy analysis. We hereby report new additional evidences confirming the result from transmission electron microscopy (TEM), high-resolution TEM, energy dispersive X-ray analysis, electron energy loss spectroscopy and selected area electron diffraction.

1. Introduction

Chemical vapor deposition (CVD) diamonds are engineering materials of great technological interest due to an exceptional combination of superior physical properties [1–5]. The integration of CVD diamonds with other technologically important materials, such as polymers and semiconductors, in a wide range of applications such as heat-spreaders in micro- and nano-electronics, for central processor units for instance, and hard and corrosive resistant hermetic coatings for medical implants and bio-electronic devices is presently not possible due to the too high substrate temperature required to synthesize diamond, typically above 400 °C. Earlier reports on low temperature diamond growth using various techniques [6–14] remain controvertible due to the intrinsic difficulties to obtain reliable temperature measurements in the non-equilibrium CVD process and the lack of evidence of deposition on low melting point materials (≤400 °C), such as polymers. Therefore, their scientific and technologic impact has remained limited. So called diamond-like carbon (DLC) materials such as tetrahedral amorphous carbon (ta-C), hydrogenated ta-C (ta-C:H) and nitrogenated ta-C (ta-C:N), can be deposited on low melting point materials such as polycarbonate at near room temperature [15–19]. However, their physical properties do not systematically compete with those of nanocrystalline diamond [4,15]. Diamond film deposition at lower substrate temperatures is therefore of considerable interest.

An important breakthrough in the resolution of this issue was recently published by Piazza and Morell [20]. They demonstrated for the first time the growth of diamond nano-crystals on polymer film by sulfur-assisted hot-filament CVD technique (HFCVD). They unambiguously showed that the substrate temperature was below 360 °C, the material glass transition temperature. The substrate temperature was estimated to be of around 250 °C. They also showed the growth of diamond micro-crystals on molybdenum at around 270 °C [20]. This accomplishment has opened the door to employ diamond in a wide range of applications where it needs to be integrated with temperature sensitive materials.

The results presented in Ref. [20] rely on visible Raman spectroscopy analysis. We hereby report new additional evidences confirming the growth of diamond on polymer at low substrate temperature from transmission electron microscopy (TEM), high-resolution TEM (HRTEM), energy dispersive X-ray analysis, electron energy loss spectroscopy and selected area electron diffraction.

2. Experimental details

The diamond synthesis experimental details were previously published [20]. Briefly, round 25-mm diameter substrates were prepared from 125-μm thick Kapton® VN foil from Dupont. Kapton® VN is a polyimide with dimensional stability up to the 360 °C [21]. A 70 nm-thick Mo layer was sputtered on these polyimide substrates to avoid hydrogen radical-induced damage to their surface during CVD process and also to avoid diamond signature masking from kapton signal in Raman spectra [20]. The substrates were seeded by sonication in a methanol suspension of high-purity diamond nanopowder from Nanodiamond (5 to 10 nm average grain size). They were then ultrasonically cleaned in methanol, dried in air at room temperature, and attached to a copper substrate holder with silver paint. The HFCVD system [22] was evacuated to 8×10^{-6} mbar before admitting the

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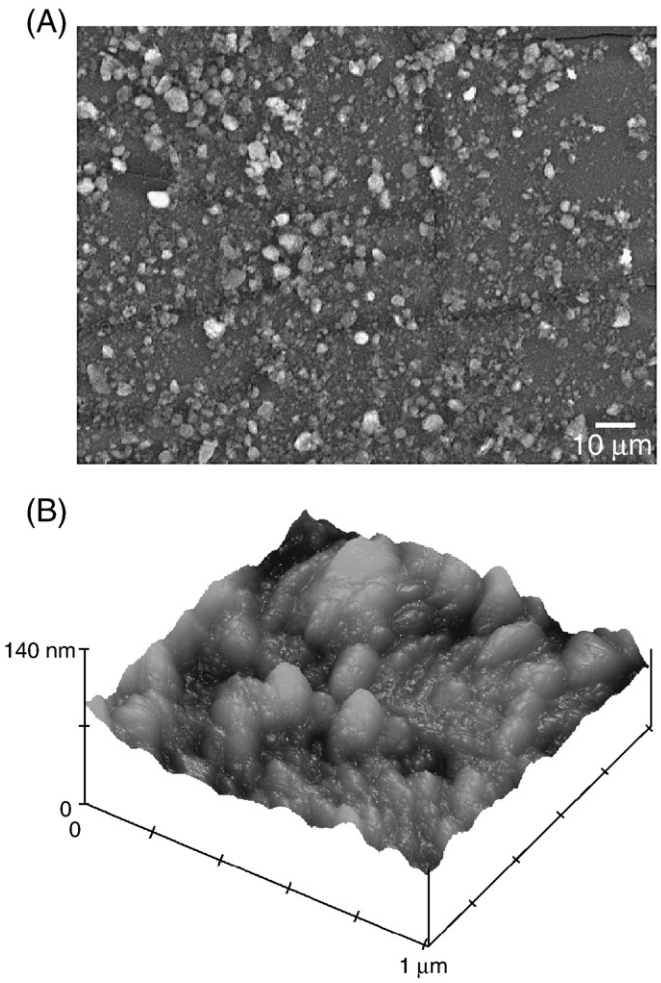

Fig. 1. (A) Representative SEM micrograph and (B) Typical three dimensional AFM image of diamond nanocrystals agglomerates deposited at sub 360 °C substrate temperature.

reactive gas mixture consisting of 0.3% CH_4 diluted in H_2 containing 500 ppm of H_2S. The total gas pressure and gas flow were kept at 27 mbar and 100 sccm, respectively, during growth. The substrate holder was fluid-cooled (50% water, 50% glycol at −10 °C) during deposition. The temperature at the substrate surface was monitored with a K-type thermocouple (exposed junction, high-temperature sheathed wires, from Omega) [20]. Details about the temperature measurements and correction can be found in Ref. [20]. The rhenium filament was positioned 12 mm above the substrate and kept at 2360 °C, as measured with a dual-wavelength optical pyrometer, resulting in a nominal substrate temperature ~250 °C, well below the glass transition temperature of polyimide [20]. The deposition proceeded for 34 h.

The surface morphology was investigated by scanning electron microscopy, SEM (JEOL Model 35 CF), and tapping mode atomic force microscopy in air, AFM (Nanoscope III, Digital Instruments). Details about AFM measurements can be found in Ref. [20]. Etched silicon cantilevers and tips were used (TESP series probes from Veeco). The tip had a radius of curvature <10 nm. The cantilever was routinely replaced to avoid imaging artifacts due to tip aging. Lateral resolution was of ~10 nm.

Raman spectroscopy was used to analyze the structure. The spectra were recorded with a triple monochromator (ISA J-Y Model T64000) using the 514.5 nm line of Ar laser and a ×80 objective. The probed area was of ~2 μm^2. The laser power on the sample and acquisition time were of 3 mW and 1000 s, respectively. Under these conditions, kapton and seeded substrates are damaged. Silicon was used to calibrate the peak position.

Transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX), electron energy loss spectroscopy (EELS) and selected area electron diffraction (SAED) were performed using an energy-filtered LEO-922 OMEGA microscope equipped with an Omega filter and EDAX Genesis 2000 microanalysis system (accelerating voltage of 200 kV) to further analyse the structure. For this purpose, 3 nm thick holly carbon coated Cu grids were prepared by scratching the samples with a commercial diamond tip. For SAED analysis, camera constant was obtain from the SAED data of a polycrystalline Al standard sample taking into consideration relativistic effects of the wavelength of electrons (of 2.508 pm) at an acceleration voltage of 200 kV [23]. High-resolution TEM (HRTEM) images were obtained using a Field Emission Gun (FEG) Philips CM 200 microscope operating at 200 kV. For this purpose, cross-section specimens were prepared following conventional techniques [24] and using a 9310 JEOL focused ion beam (FIB) equipped with a gallium gun and operating at 30 kV.

3. Results and discussion

As previously reported [20], SEM clearly shows the formation of micron and sub-micron scale clusters (Fig. 1A), as well as open areas on the substrate surface. These clusters were not observed on the seeded and cleaned substrate before deposition. They are formed during the CVD process. Clustering is promoted by the low surface mobility at sub 400 °C temperatures. The structural details of these clusters are revealed by AFM (Fig. 1B). It shows that the aggregates consist of micro- and nano-sized grains with no apparent preferential growth morphology.

In order to determine the structure of the above-described clusters, micro-Raman spectroscopy measurements were performed as previously reported [20]. The main results obtained are summarized below. The Raman spectra show a band at 1322 cm^{-1} (Fig. 2) that is redshifted and broadened compared to that of microcrystalline diamond. The Raman spectra of the seeded substrate before deposition do not present such pronounced band clearly indicating that the feature is characteristic of the material grown during CVD process. The redshifting and broadening observed can be assigned to phonon confinement, indicating that the clusters observed in the microscopy images are composed of sub 10-nm diamond nanocrystals [25]. Two other Raman features (Fig. 3) compatible with this assignment are also present: the G band at ~1600 cm^{-1}, due to the bond stretching of all pairs of sp^2-carbon [26] that are co-deposited with nanocrystalline diamond, and the band located at ~1230 cm^{-1}, due to transpolyacetylene (TPA) chains mode

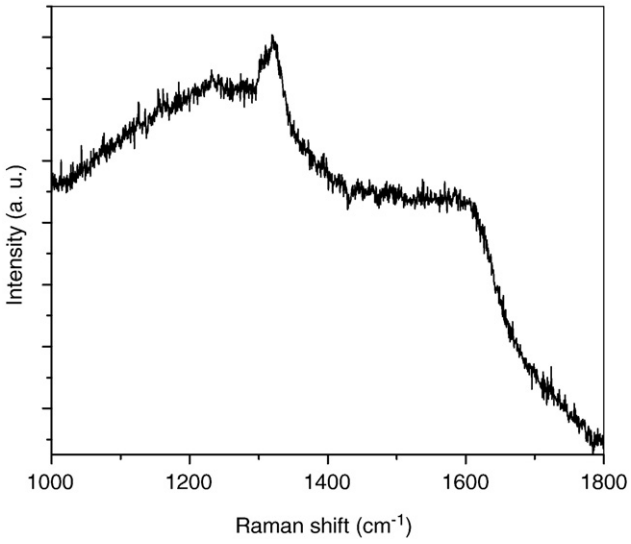

Fig. 2. Characteristic Raman spectrum of diamond nanocrystals agglomerates deposited at sub 360 °C substrate temperature.