Study on low temperature growth and formation mechanism of hexagonal diamond

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ABSTRACT

Synthesis of hexagonal diamond on Al/Ni coated thermally oxidized SiO_2 covered Si wafer substrate with photo-enhanced chemical vapor deposition (CVD) method at 450 °C is reported here. The Raman spectroscopy on grown samples shows a 1322 cm^{-1} peak with 75.4 cm^{-1} full width at half maximum (FWHM). The X-ray diffraction (XRD) data shows hexagonal diamond peaks. Various stages of hexagonal diamond formation are observed in the scanning electron microscope (SEM) images. Based on these images, a mechanism of hexagonal diamond nucleation and growth is proposed.

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1. Introduction

Super hard materials are desirable for many applications such as coatings in cutting and drilling tools. Hexagonal diamond, an allotropic form of carbon, is a super hard material with extensive potential applications in high power devices, heat sinks, and UV light sensors, among other uses. However, limited information is currently available on hexagonal diamond because of difficulties in synthesizing the material. A better understanding of hexagonal diamond synthesis mechanism is of significant interest. Several methods have been employed to obtain hexagonal diamonds to date including static-pressure [1], shock-compression [2], shock wave impulsion [3], pulsed laser impulsion [4], microwave plasma enhanced chemical vapor deposition (CVD) [5] and hot filament CVD method [6]. In general, hexagonal diamond is synthesized by applying high pressure and temperature to hexagonal graphite (HG). Khaliullin et al.'s simulations indicate that physical methods need extremely high pressure (>12 GPa) and high temperature (~1000 °C) [7]. The CVD method does not need such extreme conditions but has difficulty in obtaining hexagonal diamond exclusively. The hexagonal diamond synthesized by CVD is found with other carbon allotropes such as cubic diamond, graphite and amorphous carbon [8,9]. These syntheses typically require high temperature (~800 °C) and specially treated substrate surface such as nanocrystalline diamond or strained h-GaN film. Furthermore, the growth mechanism of hexagonal diamond formation is still not known. In this

report, we show the synthesis of hexagonal diamond of high allotropic purity at low substrate temperature of 450 °C on a thermally oxidized silicon (Si) substrate by utilizing photo-enhanced CVD. Thin films of aluminum (Al) and nickel (Ni) are deposited as catalysts on the oxidized silicon substrate. A mechanism for hexagonal diamond formation is proposed by examining scanning electron microscope (SEM) pictures that correspond to various stages during its growth.

2. Experiment

The photo-enhanced CVD system is custom-made for this experiment. The system consists of a growth chamber, gas flow system, a light source and a vacuum pump. Growth chamber has an optical window for allowing incident light to enter the chamber. The optical window is made of 1.875 inch diameter and 0.375 inch thick fused silica. The window is UV grade and has over 86% transparency for light with wavelengths between 200 and 2400 nm. Xe arc lamp is used as a light source. The output of this lamp is in 200–2400 nm wavelength range. Argon of 99.999% purity is used as the carrier gas in this work. Carbon tetrachloride (CCl_4) of 99% purity is used as the precursor. Ammonia gas of 99.999% purity is used as the annealing ambient to assist nanoparticle formation from the catalyst thin film. Bubbler is used for obtaining CCl_4 vapor and mass flow controllers are used to control the flow of Ar and ammonia gasses. Ar is used as the carrier gas to transport the precursor molecules from the bubbler to the growth chamber. The substrate holder is made of 1 in. diameter graphite cylinder. The substrate holder with a graphite cover lid contains a type K thermocouple and a heater, which is connected to a temperature controller. A rotary mechanical pump is utilized at the exhaust to control the chamber pressure. A foreline trap is used to block the oil backflow from the

mechanical rotary pump. A pressure transducer is employed for chamber pressure measurement and control.

Catalyst metal layer sandwich is deposited on thermally oxidized silicon substrates by an electron beam evaporation process. The metals are deposited under 10^{-7} Torr. A three-layer Al/Ni/Al sandwich structure composing of Al top and bottom layers and a middle Ni layer is used in this work as a catalyst. The thickness of both the top and the bottom Al layers is 5 nm and that of the middle Ni layer is 3 nm. The sample with catalyst layers is annealed at 450 °C at 10 Torr chamber pressure in ammonia ambient for 25 min. The deposition process is started immediately following the annealing cycle by commencing the flow of CCl_4 precursor in the chamber with Ar gas and simultaneously turning on the light source for 1.5 h. The deposition conditions are 450 °C substrate temperature and 10 Torr chamber pressure. The ratio of CCl_4 to Ar partial pressure during deposition process is 1:9.

3. Results and discussion

3.1. Raman spectroscopy

Raman spectroscopy is a useful method to characterize carbon materials since different carbon allotropes show different Raman spectra peaks. Single crystal of graphite has a peak approximately at 1580 cm^{-1} (G band). However, sp^2 carbon materials generally show D and G bands at the same time. The D band appears around 1350 cm^{-1} and is the disorder-induced band of sp^2 carbon materials. In general, Raman spectra peaks of hexagonal diamond can be distinguished from the peaks of cubic diamond. Cubic diamond has a single peak at approximately 1332 cm^{-1} and a narrow FWHM value while hexagonal diamond shows a single peak between 1315 cm^{-1}– 1326 cm^{-1} [10] and a broad FWHM value.

Fig. 1 is Raman spectra of hexagonal diamond sample grown in this work. Raman spectra were measured on a LABRAM Integrated Raman Spectroscopy System. A 632.81 nm HeNe laser is used as the excitation source. The Raman spectra show a peak at 1322 cm^{-1} with a FWHM value of 75.4 cm^{-1}. This peak and FWHM indicate that the sample grown is a hexagonal diamond [11].

3.2. X-ray diffraction (XRD) analysis

X-ray diffraction data is useful to define crystal structure by measuring interplanar spacing. X-ray diffraction measurements are made at the synchrotron ring of J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices (CAMD), Louisiana State University with monochromatic X-ray wavelength of 1.48 Å.

Fig. 2 shows the XRD data taken on the grown samples. The peak at 23.5° corresponds to 0.363 nm interplanar spacing which is close to 0.36 nm of carbon onion d-spacing [12]. The two peaks at 31.8 and 34.2 correspond to 0.269 and 0.251 nm interplanar spacing, respectively, and they are close to 0.27 and 0.25 nm d-spacing of AlN (1100) and (0002) plane, respectively [13]. The presence of AlN peaks in the X-ray diffraction data is attributed to Al catalyst used along with NH$_3$ in the annealing cycle. The three peaks at 39.4, 47.7 and 59.5° correspond to 0.219, 0.189 and 0.149 nm interplanar spacing, respectively, which can be attributed to 0.219, 0.192, and 0.150 nm d-spacing of hexagonal diamond (100), (101) and (102) plane, respectively [14]. We are currently not able to identify the peak at 52.1° with 0.168 nm of interplanar spacing.

3.3. SEM images of various stages

Fig. 3 shows SEM pictures at different stages of hexagonal diamond platelet growth. These geometrical progression images of hexagonal diamond formation provide a clue for mechanism of its growth. Fig. 3a corresponds to an early stage of the hexagonal diamond formation consisting of radial spokes like frame structures. Fig. 3b shows what is presumed to be the formation of graphene layers along the peripheral directions starting from the edges of the radial frame structures. This presumption is based on the differences between the observed morphology of this thin layer and the subsequent thicker grown layer above it. The hexagonal diamond-graphene layer hybrid structure has been examined in some detail elsewhere [15–17]. Comparing Fig. 3b to a, it is apparent that the growth in the radial direction of the hexagonal diamond occurs first followed by synthesis of presumably several layers of graphene along the peripheral directions providing a hexagonal boundary shape. The inner peripheral layer is completed in Fig. 3b creating empty space between two adjoining radial arms. Fig. 3c shows the connection of two radial arms with layers of graphene. Although these peripheral layers of graphene grow from two different radial arms, there does not appear to be a discontinuity in the connected graphene layers. This indicates that the lengths of the adjoining diagonal frames are equal and the angles between the diagonal frame on either side and the graphene layers forming on that side are also the same. This is consistent with the assumption that the starting point of the hexagonal diamond platelet growth is at the center and the growth rate of each radial arm is the same. Fig. 3d is a more detailed image than Fig. 3c and shows filling of empty spaces between the peripheral layer and the diagonal arms. The proposed mechanism stipulates growth of graphene
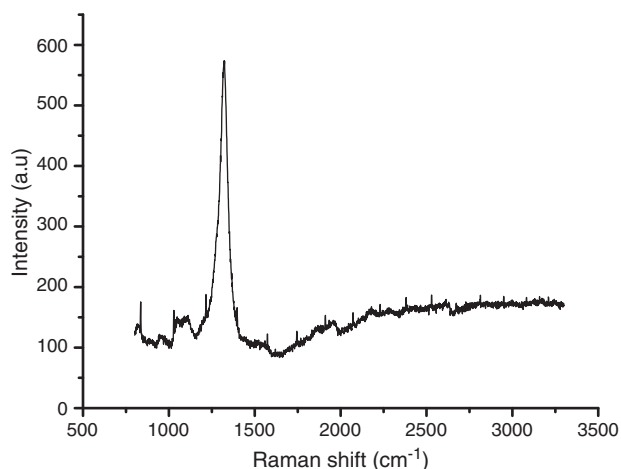

Fig. 1. Raman spectroscopy data on deposited samples indicating hexagonal diamond growth.
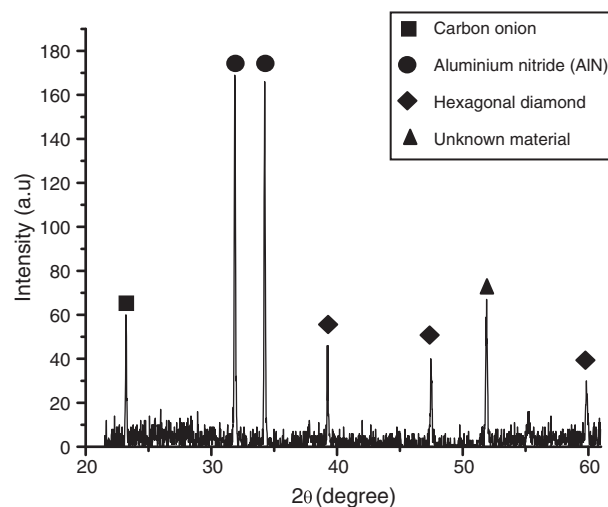

Fig. 2. XRD data on hexagonal diamond sample.