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Short communication

The synthesis of diamond films on adamantane-coated Si substrate at low temperature

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ABSTRACT

Diamond films have been synthesized on the adamantane-coated Si (1 0 0) substrate by microwave plasma chemical vapor deposition from a gaseous mixture of methane and hydrogen gases with a growth rate of ~6.7 nm/min. The substrate temperature was ~475 °C during diamond deposition. The films obtained have good crystallinity that is characterized by scanning electron microscopy and Raman spectrometry. X-ray photoelectron spectroscopy analysis has confirmed that diamond nucleation and growth are on SiC rather than clean Si. The possible mechanism of high rate growth diamond films has been demonstrated.

1. Introduction

Recently, the synthesis of diamond at low temperature has attracted much attention of materials scientists, owing to its wide range of applications in optics, microelectronics, tribological, thermal management, biomedical, DNA-based sensor, and manufacturing engineering [1–4]. The exceptional physical and chemical properties of diamond such as wide band gap, chemical inertness, high carrier mobility, excellent biological compatibility, high propagation speed of acoustic wave, good optical transparency, high thermal conductivity and the greatest hardness that make its use advantageous in a wide range of applications [5–7]. Several methods have been proposed for the synthesis of high crystalline diamond films by microwave plasma chemical vapor deposition (MPCVD) at high temperature and pressure [7–13]. However, to make commercially viable further investigations are still required in terms of yield, quality and uniformity of diamond. In addition, the synthesis of high quality and better crystalline diamond film at low temperature and pressure is still challenging.

In the present study, we introduce adamantane ($C_{10}H_{16}$), a series of carbon structure for the diamond nucleation. Adamantane can sublime easily and has a relatively high vapor pressure. It is the smallest unit cage structure of the diamond crystal lattice, consisting of 10 carbon atoms arranged as a single diamond cage [14,15], surrounded by 16 hydrogen atoms, as shown in Fig. 1(iii). In this molecule, the angles at carbon atoms are fairly close to the tetrahedral and C–C single bond has a length of 1.54 Å. Partial collapse of adamantane molecules is known to yield carbon clusters (C_nH_x) where $n = 3, 5, 6, 7, 8$ and 9 of significant abundance [16]. To the best of our knowledge, this is the first report showing the synthesis of diamond films on the adamantane-coated Si (1 0 0) substrate at low temperature.

2. Experimental methods

The schematic diagram of deposited adamantane on Si substrate by hotplate method is shown in Fig. 1. The synthesis processes of the diamond films is consisted of the following steps: a mirror-polished p-type (1 0 0) Si wafer with dimensions of 1 cm × 1 cm without any mechanical pre-treatment were used as the substrates. The Si substrates were ultrasonically cleaned consecutively in acetone and alcohol for 10 min, and dried with N_2 spray. Subsequently, cleaned substrates were dipped in buffered oxide etch solution for 5 min to remove the native oxide layer from the Si substrates. Further, the cleaned Si substrate was mounted onto the crystalline adamantane powder and placed on the hot plate at 250 °C for 5 min (here after called hotplate method). At high temperature adamantane sublimed immediately and thick adamantane layer deposited on the Si substrate. Manually, we measured the thickness of deposited adamantane by scale, it was approximately ~0.9 mm. The deposited adamantane on Si substrate was then placed on a Mo-disk holder for diamond synthesis. The deposition of diamond was carried out in 1.5 AsTeX-type microwave plasma chemical vapor deposition (MPCVD) system. The microwave power, pressure, total gas flow rate, deposition time, and the temperature were fixed at 300 W, 20 Torr, 200 sccm, 270 min, and 475 °C, respectively. The temperature was measured by optical spot pyrometer. Finally, the samples

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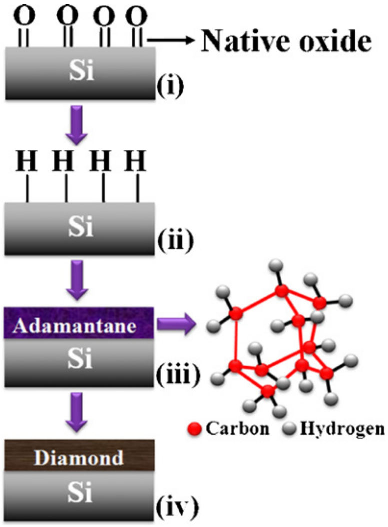

Fig. 1. Schematic diagram showing diamond synthesis in four steps; (i) silicon substrate with native oxide layer, (ii) BOE solution for 5 min to remove native oxide from the Si surface by hotplate method, (iii) adamantane deposited on silicon surface, and (iv) diamond growth by MPCVD.

were allowed to cool down to ambient temperature in the presence of hydrogen gas (10 Torr) to etch with hydrogen plasma of nondiamond phases that remained after the diamond growth. To study the role of adamantane in diamond growth, we prepared another sample without adamantane-coated Si substrate. The diamond growth conditions were similar to that of adamantane-coated Si substrate.

3. Results and discussion

After coating of adamantane on Si substrate by hotplate method, the atomic force microscope (AFM, D3100) was used to evaluate the surface morphology of adamantane-coated (AC) Si substrate, as shown in Fig. 2(a). Here, we used tapping-mode AFM on a length scale of 2.5 μm × 2.5 μm to determine the surface roughness of the adamantane films. The average particles size of adamantane seems to be a ~100 nm. Fig. 2(a) indicates that the surface roughness of the adamantane film surface was ~2.92 nm. In addition, the AC Si substrates were evaluated by Raman spectroscopy (LABRAM HR 600). The Raman spectra were acquired with a micro-mode using an Ar laser beam which was focused to ~1 μm diameter. Intense Raman peaks in the range of 1000–1800 cm^{-1} is shown in Fig. 2(b). We observed multiple Raman peaks of AC/Si at 1095, 1120, 1220, 1312, 1432 and 1509 cm^{-1}, as shown in Fig. 2(b). These peaks were obtained due to different modes of hydrocarbon (HC). The Raman peaks at 1095, 1120 and 1220 cm^{-1} was due to doubly-degenerated CH wag/CH_2 twist modes and another Raman peaks at 1432 and 1509 cm^{-1} may be due to E CH_2 scissor mode [17]. While the weak Raman active A_{1g} mode at 1312 cm^{-1} exhibits a hexagonal nanodiamond phase [18,19].

Further, the AC and without adamantane-coated (WAC) Si substrates were placed in the MPCVD reactor for diamond deposition. The structure, surface morphology, and size of the synthesized diamond on the Si substrate were examined with field-emission scanning electron microscopy (SEM, JEOL JSM-6700F). Fig. 3(a) and (b) shows a typical plane view and cross-section SEM images of synthesized diamond on the AC/Si substrate. The aim was to use adamantane as a seed for the nucleation and growth of diamond on a Si substrate. We observed the average size and the thickness of synthesized diamond were ~2 and ~1.8 μm respectively, as shown in Fig. 3(a) and (b). To know the effect of adamantane nucleation in diamond synthesis, we have grown the diamond on the WAC/Si substrate under the same experimental conditions as AC. The morphology of synthesized diamonds of WAC is shown in Fig. 3(c) and (d) that shows a local region where we observed the highest diamond density. Most of the areas of WAC are rarely observed diamond particles. We observed the average size and the thickness of synthesized diamond were ~1 and ~0.9 μm, respectively [size may not be the focus, it is the density]. From these results, we observed the growth rate of diamond was ~6.7 and ~3.3 nm/min for AC and WAC, respectively. Thus, the growth rate AC diamond was two times faster than WAC diamond. We have also observed the density of diamond was ~10^6 and ~10^2 cm^{-2} for AC and WAC respectively, clearly indicates that the density of AC diamond is higher than that of WAC diamond, by four orders. We have noticed that the adamantane nuclei not only increased the quality, crystallity, and growth rate but also enhanced the yield of diamond at low temperature.

Adamantane is the smallest unit of diamondoids (recent discovery of previously inaccessible quantities of nanometer-sized hydrogen-terminated diamond clusters, also known as diamondoids) [20,21]. It is also well known that the adamantane serves as embryos for nucleation of diamond in the gas phase. As a result, when the AC substrate exposed to diamond growth environment, adamantane molecules desorbed from the Si surface and mixed with gaseous (0.6% CH_4 in H_2) plasma. It gives the crucial information about convert of nuclei to crystalline diamond. Probably, during the process of mixing with gaseous plasma, the adamantane

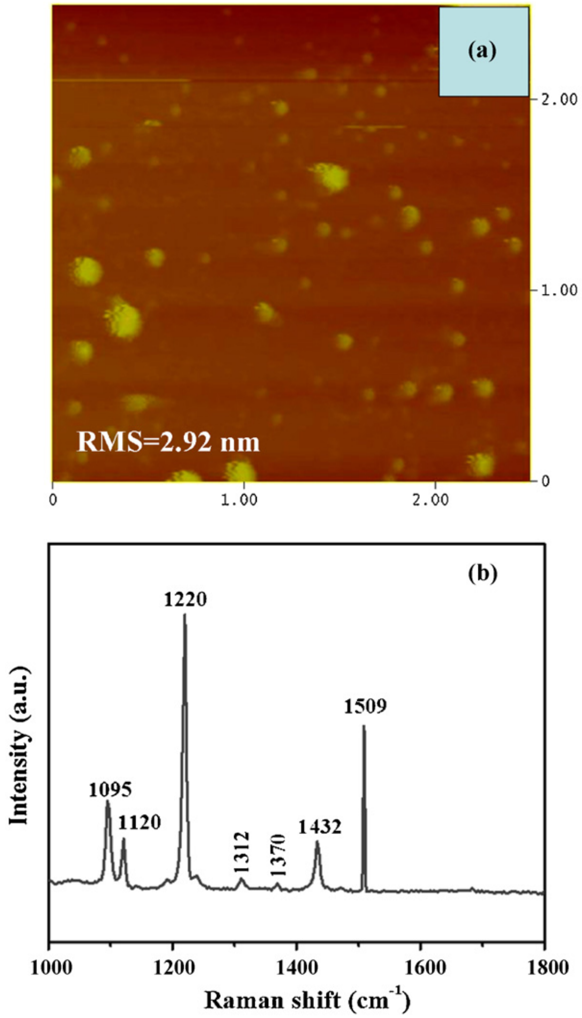

Fig. 2. (a) Tapping-mode AFM image and (b) Raman spectrum of AC/Si.

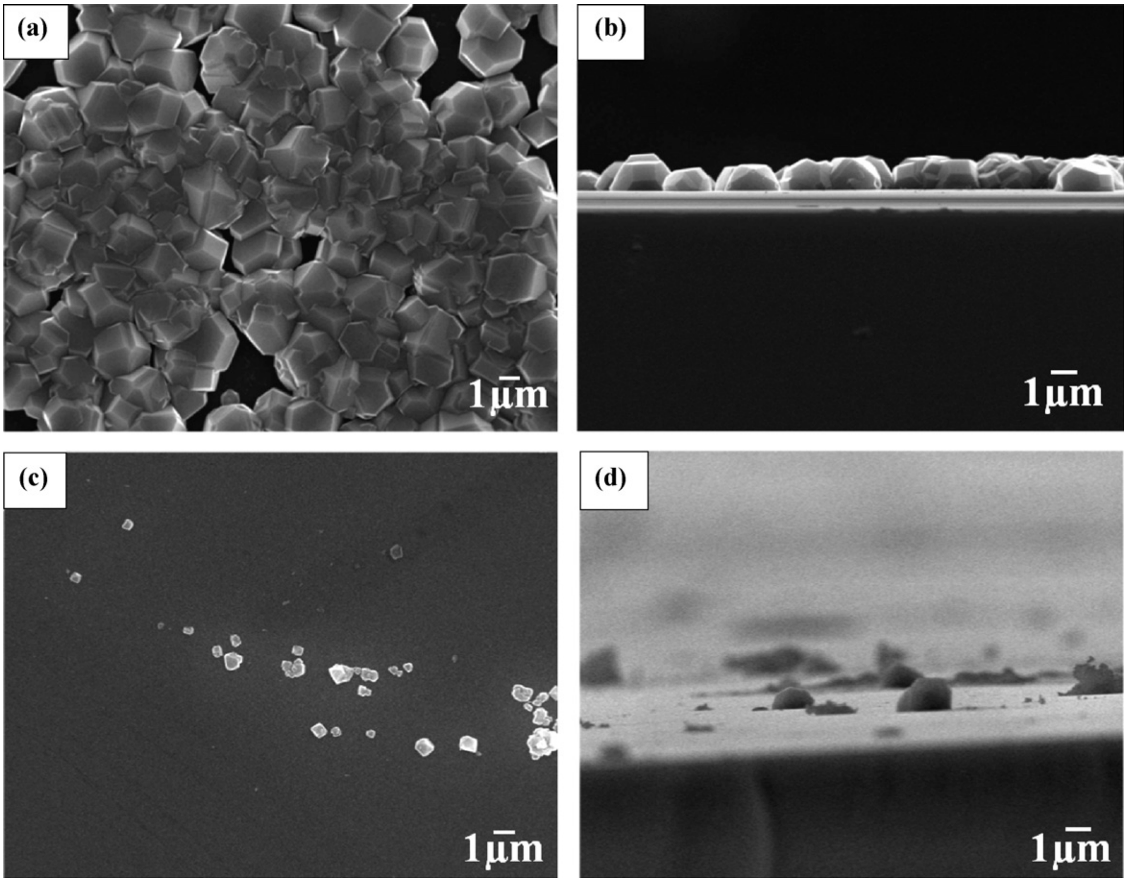

Fig. 3. SEM image of diamond: (a) plane view of AC, (b) cross-section view of AC, (c) plane view of WAC and (d) cross-section view of WAC.

molecules would be decompose into hydrocarbon species. These molecules are further converted into crystalline carbon particles by chemical and physical reaction such as, the formation and migration of molecules in the vicinity of surface, hydrogen abstraction, dehydrogenation of absorbed complexes, recombination of hydrogen atoms, etc. The deposited crystallized particles can act as nuclei for the subsequent growth of diamond on the Si substrate. After nucleation, methane (0.6%) gas species may facilitate the growth of three dimensionally individual nuclei. To better understand the nucleation and growth mechanism of diamond from adamantane molecules, we have studied the AC/Si substrates with pure hydrogen plasma treated for different times (1, 2, 5, 10 and 15 min) at same experimental condition. After treated times, the samples were evaluated by Raman spectroscopy, as shown in Fig. 4. We observed the nanodiamond signal at 1150 and 1460 cm^{-1} after 1 min treated with pure hydrogen plasma. A number of authors have found either the 1150 or 1460 cm^{-1} peak by themselves. It is very clear that whenever the 1150 cm^{-1} peak is observed, nanodiamond phase, either in the cubic form or in the hexagonal form is observed in both the XRD pattern and by transmission electron microscope [22–25]. Other multi-Raman peaks (954, 1050, 905, 941, 982, 998 and 1022 cm^{-1}) at different treating times (1, 2 and 5 min) may come from hydrocarbon species of adamantane (study is still underway). The peak at 1480 cm^{-1} is also comes nanodiamond phase. Marcus et al. and Zhang et al. have noticed that the peak at 1480 cm^{-1} is attributed to a tetrahedrally bonded carbon phase [26,27]. While other peaks at 1606 and 1350 cm^{-1} are observed in 10 and 15 min, respectively. The peaks at 1350 and 1606 cm^{-1} are the D and G modes, respectively attributed to disordered graphitic phase. It seems that after 15 min treated with pure hydrogen plasma, most of the hydrocarbon species have been etched out. From Raman studies it is clear that adamantane may be decompose into hydrocarbon species, which act as individual diamond nuclei at low temperature. And then may be CH_4 gas species may facilitate the growth of three dimensionally individual nuclei. Often some degree of nondiamond carbon is incorporated during nucleation. The atomic hydrogen or ions prevent the formation of nondiamond carbon impurity on the surface. Study of the mechanism behind the origin of diamond nuclei from adamantane molecule is still underway in our laboratory.

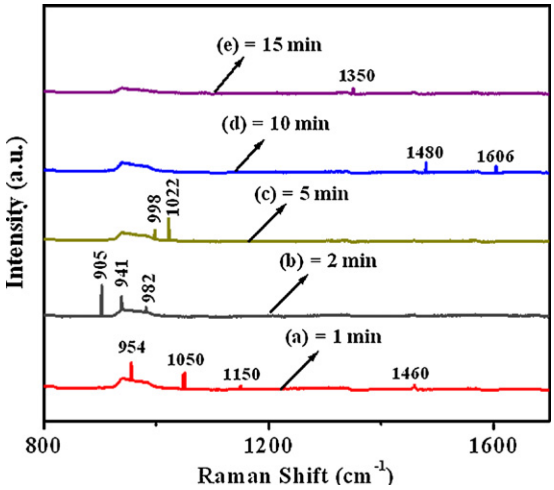

Fig. 4. Raman spectrum of AC/Si treated with pure hydrogen plasma at different times (1, 2, 5, 10 and 15 min).

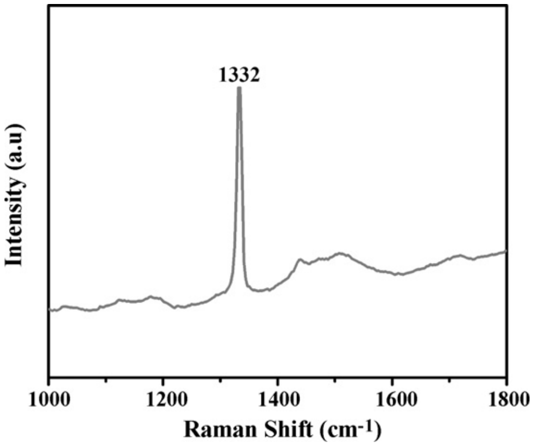

Fig. 5. Raman spectrum of after 270 min diamond growth.

Furthermore, the synthesized diamond films on the AC/Si substrate were evaluated by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS, Thermo VG 350, MgKα X-ray source). After diamond growth on AC/Si, we noticed that all adamantane peaks are converted into a sharp Raman peak at 1332 cm^{-1}, as shown in Fig. 5. However, we did not observe nanodiamond peak at 1150 cm^{-1}. It seems that diamond growth on AC/Si substrate from gaseous plasma (0.6% CH_4 in H_2) is favour to form the micro-diamond film. The band at 1332 cm^{-1} in Raman spectra is attributable to the first-order phonon mode for diamond. The width of the peak gives an insight of the crystallinity of the diamond. We determined the width of AC/Si diamond peak is 5.6 cm^{-1}. The sharp Raman peak at 1332 cm^{-1} and the absence of graphitic (D and G bands) peaks suggest that the good-quality diamond is obtained. This is consistent with our SEM observation, as shown in Fig. 3(a) and (b).

In addition, to get a better insight into the above mechanisms, we have used XPS to characterize the surface chemical composition of the AC/Si surface after diamond growth. The XPS survey spectrum of the synthesized diamond on the Si substrate is shown in Fig. 6, which allows measure of the carbon 1s core-level signal considered as an indicator for the quantity of carbon attached to the surface treatment. Apart from the expected peaks from elements of the diamond surface (C), surface contamination with oxygen containing molecules can be detected. An XPS survey shows strong signals of carbon C 1s at 285.2 eV, attributed to the C–C bond in diamond films. In fact, inset XPS high-resolution spectrum of carbon in Fig. 6 showed the C 1s signal revealed two peaks: the first peaks at 285.2 eV is the characteristics of C–C bonding and other peak at 283.7 eV is the characteristics of C–Si bonding. Many authors have shown that silicon carbide (SiC) forms readily after diamond growth starts [28,29]. In our case, probably the presence of hydrocarbon species of adamantane reacts with Si surface and formed SiC layer. However, we believe that the SiC layer may partially effect in the growth of diamond film. The part of the oxygen signal at 532.7 eV is associated with oxide formation with Si surface during the thermal reaction. The oxygen peak at 532.7 eV attributed to the O–Si bond in SiO_2 [10,11]. We also observed the Auger peak at about 745 eV in XPS spectrum. The weak signals of silicon Si 2p and Si 2s at 99 and 151 eV, indicates that the most of silicon surface is covered by diamond films [30]. On the basis of XPS results, we confirm the existence of diamond.

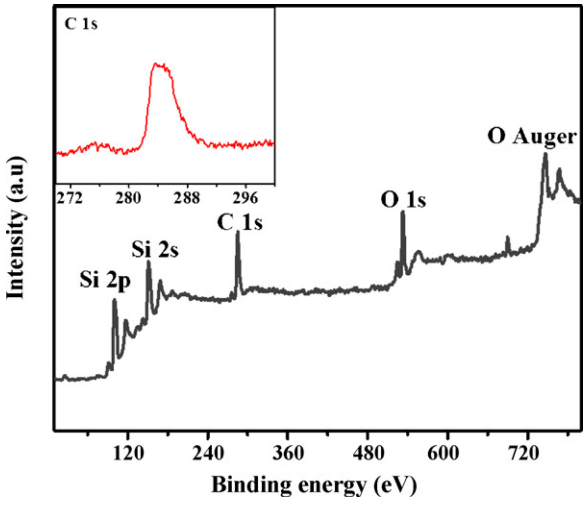

Fig. 6. The XPS survey spectrum of diamond/Si, inset: high-resolution spectrum of the C 1s region.

The purpose of this study is to establish the adamantane nucleation substrate is more effective for diamond growth at low temperature. We conclude that the adamantane nuclei not only improved the growth rate but also enhanced the density of diamond at low temperature.

4. Conclusions

In summary, we demonstrated a new, simple and efficient way to synthesize the high-quality crystalline diamond films. The results show that the presence of the adamantane molecules was found indispensable in promoting an efficient nucleation of diamond films at low temperature. Thus, the adamantane molecules may have a better future for diamond nucleation and growth at low temperature. Low temperature deposition of diamond can make it undesirable for use in critical applications.

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