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Chemical Precursor for the Synthesis of Diamond Films at Low Temperature

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In this study, diamond films have been synthesized on adamantane-coated (100) Si substrates at 530 °C by microwave plasma chemical vapor deposition from a gaseous mixture of methane and hydrogen. Scanning electron microscopy, Raman spectroscopy, and X-ray diffraction were employed to characterize the carbon chemical species on the Si substrate from adamantane into diamond. These measurements provide definitive evidence for formation of high-crystalline diamond film on Si substrate without any other pretreatments. Moreover, the possible mechanisms for the diamond formation are presented. © 2010 The Japan Society of Applied Physics

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Recently, the synthesis of diamond has attracted much attention due to its unique properties such as wide band gap, chemical inertness, high carrier mobility, excellent biological compatibility, good optical transparency, excellent thermal conductivity, high propagation speed of acoustic wave, and the greatest hardness. The unique properties of diamond make it an ideal material for a wide range of applications in optics, microelectronics, tribological, thermal management, biomedical, DNA sensor, and so on.[1–4] Many studies have been reported on the synthesis of crystalline diamond films on non-diamond substrates. Several research groups had used different nucleation steps such as scratching substrate with powder (diamond, nitride carbide, oxides, etc.), dc or ac voltage bias, and using thin film precursors (graphite fibers, fullerene, etc.) for the deposition of diamond.[5,6] However, most of these methods still requires improvement in both the yield and temperature of the diamond deposition by chemical vapor deposition (CVD).

In this report, we introduce adamantane for the diamond deposition at low temperature. Adamantane ($C_{10}H_{16}$) is one of a series of carbon structure, very stable crystalline compound. Adamantane is an interesting molecule which has a cage structure being constructed with carbon atoms, and has tetrahedral symmetry like diamond. The adamantane is categorized as the smallest possible diamondoid (chemical formula $C_{(4n+6)}H_{(4n+12)}$, where $n = 0, 1, 2, 3, \ldots$), consisting of 10 carbon atoms arranged as a single diamond cage surrounded by 16 hydrogen atoms, as shown in Fig. 1. Adamantane is hydrogen-terminated diamond molecules. It does not melt at ambient pressure but sublimates. Partial breakdown of adamantane is known to yield carbon clusters (C_nH_x), where n = 3, 5, 6, 7, 8, and 9, of significant abundance.[7,8] Another important issues particularly in CVD of diamond since early in studies is the high deposition temperature (700–900 °C), which limits only on thermally stable substrates. The deposition of high quality and better crystalline diamond at low temperature is still challenging even if some studies reported diamond deposition at temperature below 600 °C.[9–11]

In this study, we report a simple and easy method for the synthesis of good-quality diamond film on adamantane-coated Si substrate by the microwave plasma chemical vapor deposition (MPCVD) at relatively low temperature. The advantages for using the adamantane are that it is not much expensive and easily commercially available.

The synthesis processes of the diamond are described as follows: Mirror-polished p-type (100) silicon wafers with dimensions of 1 × 1 cm^2 without any mechanical pretreatment were used as the substrates. The substrates were ultrasonically cleaned with acetone and alcohol for 10 min respectively, and then high-pressure N_2 gas was used to remove the any remaining particles from the Si surface. The cleaned samples were dipped into buffer-oxide-etch solution (10% HF) for 5 min to remove the native oxide layer from the Si surface. Further, the cleaned Si samples were fixed onto a ceramic plate. The adamantane powder was kept in a ceramic crucible and covered with fixed Si ceramic plate, and then placed on a hot plate at 250 °C (hereafter called hot-plate method) for 300 second, which allowed adamantane to coat onto the Si surface. The distance between the fixed Si substrates and adamantane powder was ~2 mm. The thickness of deposited adamantane on Si was manually measured by scale, it was approximately ~0.9 mm. The adamantane-coated Si substrate was then placed on a Mo-disk holder for diamond growth in an AsTeX-type MPCVD system. The detailed processing parameters for MPCVD are as follows: the total pressure was 20 Torr, the microwave power was 350 W, the total flow rate was 200 sccm, deposition time was varied from 15 to 270 min, and the temperature was ~530 °C as measured by an optical pyrometer. To evaluate the effect of adamantane on diamond nucleation and growth, we prepared another Si substrate sample without adamantane-coating. The same MPCVD deposition conditions were applied for comparison.

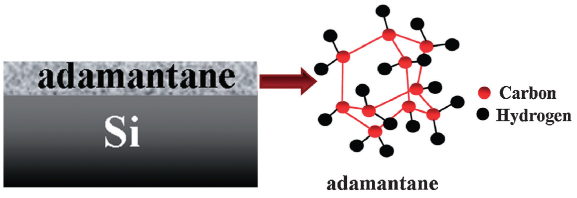

Fig. 1. Adamantane deposited on silicon surface by hotplate method.

The adamantane-coated Si substrates were placed in a MPCVD reactor for diamond synthesis. In the MPCVD reactor, the plasma was formed by activating the mixture of gases (0.6% CH_4 in H_2). To explore the diamond nucleation and growth from adamantane molecules, MPCVD were carried out for various deposition times (15 to 45 min) on adamantane-coated Si substrate. The field-emission scanning electron microscope (FE-SEM; JEOL JSM-6700F) image in Fig. 2(a) shows that a number of tiny particles in micrometer size are formed after 15 min deposition. The inset high-magnification image in Fig. 2(a) shows that the tiny particles

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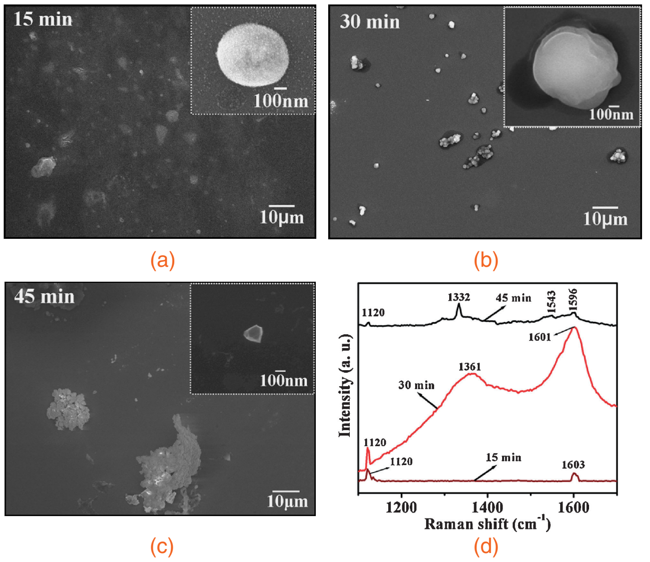

(a) (b) (c) (d)

Fig. 2. Plan-view SEM images and micro-Raman spectra after growth for deposition times of (a) and (c) 15 min, (b,d) 30 min, and (c,f) 45 min.

are surrounded by several hundred nanometer-sized particles. The micro-Raman spectrum from these particles in Fig. 2(d) shows the major peaks at 1120 and 1603 cm^{-1}, suggesting that some adamantanes may have been decomposed during deposition (15 min). Also, it is likely that adamantane molecules are sublimated from the Si substrate at 530 °C and redeposited from the plasma. Sublimation of adamantane might increase carbon supersaturation which could favorably result to the formation of sp^2 phase. The Raman peak at 1603 cm^{-1} is the G band of sp^2 carbon bonding, while the 1120 peak is not well understood about the bonding characteristics but it is often observed in Raman spectra of nanocrystalline diamond films,[12–14] suggesting that nanostructured diamond particles can be formed from adamantane molecules. Previous studies have shown that the peak at 1120 cm^{-1} usually appears for nanocrystals 1–2 nm in diameter or carbon clusters of sp^3 bonded material. However, this peak can also appear at 1150 cm^{-1} but only in very poorly organized graphite, being related to structures of a mixed sp^2–sp^3 nature.[15–17] It is widely believed that the peak at 1120 cm^{-1} originated from the presence of confined phonon modes in diamond. After having been decomposed, the surrounded nanosized particles were not observed (30 min deposition), instead clusters of micro-sized carbon particles formed, as shown in Fig. 2(b). The high magnification SEM image [inset in Fig. 2(b)] shows that the particles have bright contrast while the rest regions exhibit dark contrast. The Raman spectrum from these particles is shown in Fig. 2(d). We observed Raman peaks at 1120 cm^{-1} (described above), with 1361 and 1601 cm^{-1} show the D and G band, respectively. The D band (may be from dark region) peak is usually attributed to disorder carbon, showing the transformation from adamantane to sp^2, while the Raman peak at 1601 cm^{-1} shows the graphitic phase of particles. After 45 min deposition, we did not observe dark regions. We observed only clusters of carbon particles with a few nano-sized particles. It seems that after 45 min deposition the dark regions [in Fig. 2(b)] are fully transformed into graphitic phase. The high-magnification SEM image in Fig. 2(c) shows that the crystalline diamond particles have also been synthesized. The Raman spectrum from these particles is shown in Fig. 2(d), showing the multi Raman peaks at 1120, 1332, 1543, and 1596 cm^{-1}. The existence of Raman peaks at 1120 and 1332 cm^{-1} clearly supports that the diamond formation has occurred, as shown in Fig. 2(c). We observed the hydrogenated amorphous carbon (a-C:H) peak at 1543 cm^{-1} in the Raman spectrum. The Raman peak at 1596 cm^{-1} will support the graphitic phase particles. From our experimental results, it is clear that the adamantane molecules may assist diamond formation. Here, it is worthwhile to briefly discuss the possible mechanisms of diamond nucleation and growth from adamantane. One possibility is that the evaporated adamantane might decompose into individual molecules which can either remain in the gas or be removed from its surrounded hydrogen by hydrogen abstraction. The hydrogen abstraction is one of the highly possible mechanisms for diamond nucleation in the gas phase as adamantane can be considered as diamond nucleus covered with hydrogen atoms, and then methane gas species in hydrogen plasma may facilitate the growth of three dimensionally individual nuclei.[18] Alternatively, the high evaporation rate of adamantane molecules would be enhance the concentration of carbon in the plasma which favors to form the nucleation from supersaturation. Finally, probably the residue of adamantane molecules would behave as nuclei or embryos for diamond, and then carbon radicals from methane species in the plasma enhance the diamond growth. The study of the exact mechanism of diamond nucleation and growth from adamantane is still underway.

The structure, surface morphology, and size of the synthesized diamond on the Si substrate with and without adamantane coating were examined with SEM as shown in Figs. 3 and 4. Figures 3(a) and 3(b) show the SEM image and Raman spectrum from a sample deposited on Si substrate without adamantane coated after 30 min deposition. After 30 min deposition, the density of diamond crystallite is very low, and the Raman peaks are observed at 1120 and 1477 cm^{-1}, which can attribute to nanocrystals in 1–2 nm in diameter or carbon clusters of sp^3 bonded material and amorphous carbon as mentioned above. Thus, we believe that the carbon species of this peak (1120 cm^{-1}) would be responsible for the formation of micro-diamonds (without adamantane) in further deposition as shown in Figs. 3(c) and 3(d). The G-band signals are not observed in the Raman spectrum as shown in Fig. 3(b), while we observed G-band signals from adamantane-coated Si substrates. It is clear that some of adamantane molecules may have converted into the graphitic states (Fig. 2) in the plasma and it may assist to diamond nucleation. Previous studies have also shown that the graphite-seeding enhance the diamond nucleation.[19,20] Figures 3(c) and 3(d) show typical SEM images of synthesized diamond on Si without adamantane-coating. The average size and height of synthesized diamonds are ~1.2 and ~1 μm, respectively, and the density of diamond particles is ~10^3 cm^{-2}. Figure 4 shows plan-view and cross-section SEM images of synthesized diamond on adamantane-coated Si substrate after 270 min deposition. It is seen that a ~2-μm-thick continuous film with well-faceted morphology has formed, and the average size of diamond grains is ~1.6 μm. The growth rate of diamond is estimated to be

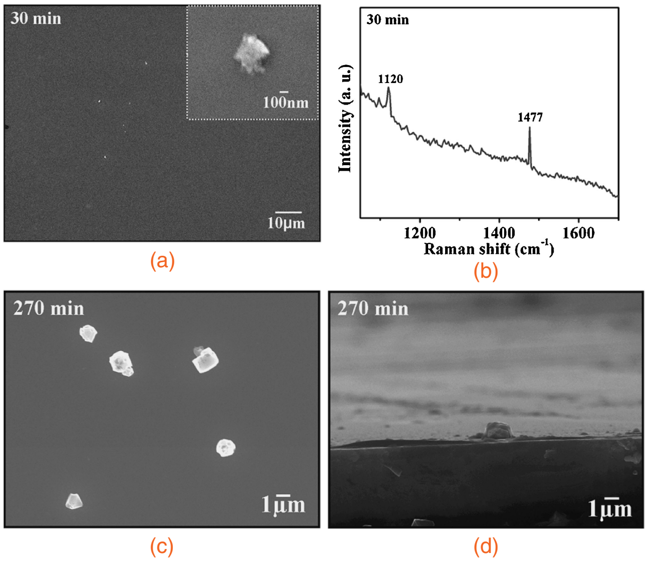

Fig. 3. SEM images and Raman spectra (a) and (b) after 30 min, (c) plan-view and (d) cross-section view of diamond (growth time 270 min) on Si without adamantane coating.

~0.5 μm/h, and the density of diamond is ~10^8 cm^{-2} on the adamantane-coated substrate. It clearly indicates that the density of diamond is higher on adamantane-coated substrate than uncoated one by five orders. Therefore, we conclude that the adamantane not only increases the quality, crystallinity, and growth rate of CVD diamond, but also enhances the yield. Further, the X-ray diffraction (XRD) pattern from the sample of 270 min deposition shown in Fig. 4(c) also supports the formation of the micro-diamond crystalline film, as we can identify one sharp peak of diamond (111) at 43.9°. In addition to Si peaks, we also notice that there is a peak at 61.7° corresponding to crystalline 3C-SiC(220).[21,22] However, we did not observe any graphite peak, implying that the graphite fraction is insignificant compared to diamond phase. Furthermore, the micro-Raman spectrum in Fig. 4(d) clearly shows the characteristic feature of diamond at 1332 cm^{-1} with the full width at half-maximum to be less than 7 cm^{-1}. The sharp Raman peak suggests that the high quality microdiamonds have been synthesized on the Si surface. The above results show that the high-crystalline quality diamond film can be synthesized on adamantane-coated Si at 530 °C. As a result, we propose that the adamantane is the indispensable candidate for nucleation and growth of diamond film on Si substrate at low temperature. The mechanism for the diamond nucleation and its growth from adamantane molecules still needs further study adamantane with the aid of high-resolution transmission electron microscopy.

In conclusion, we demonstrate a simple method for the synthesis of good quality and highly crystalline diamond film on adamantane-coated Si substrate by microwave plasma chemical vapor deposition using a mixture of methane and hydrogen gases. The results from SEM, XRD, and Raman spectroscopy show that the adamantane assists the diamond films growth. Scanning electron microscopy examination shows that on the adamantane-coated Si substrate a high-density continuous diamond film can form on Si than that of without coated which has a much lower density.

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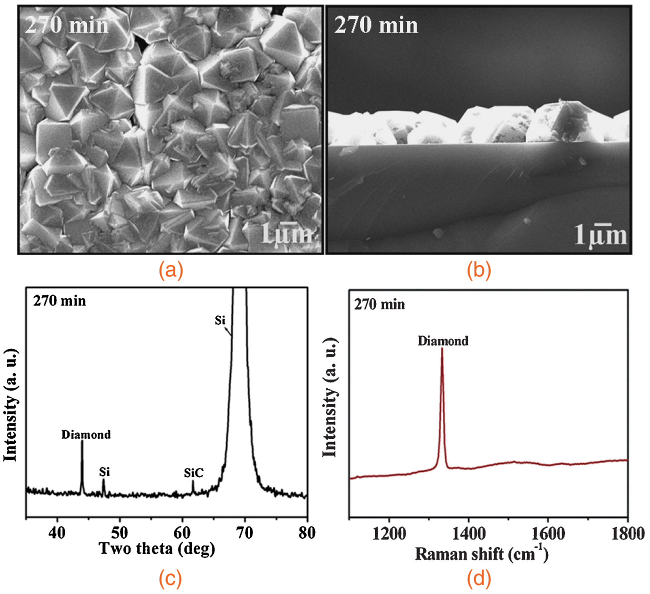

Fig. 4. SEM images of deposited diamond in (b) plan-view and (d) cross-section view, (c) XRD pattern, and (d) Raman spectrum after synthesized diamond (growth time 270 min) on Si surface coated with adamantane.

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