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Highly (111)-textured diamond film growth with high nucleation density

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Abstract In a traditional hot-filament chemical vapor deposition (HF-CVD) system, highly (111)-textured diamond film was deposited on Si (111) substrate treated by diamond powder ultrasonic scratching or other methods. The relationship between the (111)-textured diamond film growth and the nucleation density has been discussed. The morphologies and structures of the films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy.

Key words Diamond film, HF-CVD, Nucleation, Defect, Silicon carbide, Nanowire

CLC numbers TN304.1^{+}8, TN304.055, TN305.1

1 Introduction

Diamond has many excellent properties, e.g., wide band gap, optical transparency, high thermal conductivity, chemical inertness and extreme hardness, which are important for the applications in high temperature electronic devices, tool coatings, heat sinks and optics[1,2]. To capture the full utilities of the unique properties of diamond, it is necessary to deposit high quality diamond film with low cost. However, the deposition of high quality diamond film on silicon substrate has been a considerable challenge due to its low nucleation density[3-5]. To overcome the difficulty, many methods, such as seeding with diamond powders[6], abrading with silicon carbide[7], negative substrate biasing during the initial stage of deposition[8], have been successfully used. In these pretreatment methods, the nucleation is affected by many factors, e.g. the residual diamond seeds, carbon precursors, changes in surface stress， formation of carbide, etc. And mechanism of diamond nucleation is not yet clear, too. Most of researchers focused on the nano-sized defects created by diamond powder scratching or ion-beam bombardment, but few authors investigated effects of different defects on the diamond nucleation.

Moreover, highly (111)-textured diamond film has received considerable attention due to its high negative electron affinity[9]. Many methods, such as using a graphite plate as solid carbon source[10], adopting a lower-than-normal filament temperature pretreatment[11], and using Ir/CaF$_2$/Si as substrates[12], have been employed to deposit highly (111)-textured diamond films. Researchers always use different substrates and adjust the temperatures of both filament and substrate to a proper value to obtain the (111)-textured diamond films. Few people investigated the effect of diamond nucleation density on the (111)-textured growth of diamond films.

In this paper, diamond films were deposited on different silicon substrates in a typical hot-filament CVD apparatus. Effects of different defects produced

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by diamond powder scratching or scalpel scratching on the diamond nucleation enhancement are discussed.

2 Experimental

N-type (111)-oriented mirror polished silicon wafer was used as substrate. To investigate the defect effects on diamond nucleation, silicon wafer scratched ultrasonically or manually with 0.5 μm diamond powder, and silicon wafer scratched by a scalpel, were used as substrates. Also, an untreated mirror polished silicon wafer was used for comparison. The substrates placed in the CVD chamber were 8 mm to the filament. The deposition was conducted at typically 750 °C.

The chamber was evacuated to 1.0×10^{-2} Pa, and CH_4 and H_2 gases, typically in 6.0 kPa, were fed into it. While the H_2 was in a constant flow rate of 100 SCCM, the CH_4 was in flow rate of 4.0 SCCM for the first 15 min and 1.0 SCCM thereafter for different durations (up to 8 h) of the diamond film growth.

The deposited films were analyzed by scanning electron microcopy (SEM LEO, 1530VP), micro-Raman spectroscopy (Dilor LabRam-1B) and X-ray diffraction (Cu Kα, λ=0.1541 nm, D/max-2200 X-ray Diffractometer) at room temperature. The Raman spectra were obtained using an Ar^+ laser of 514.5 nm in wavelength and ~1 μm in spot size.

3 Results and discussion

Fig.1 shows typical SEM images of the films after 8 h growth on Si(111) substrates treated by diamond powder ultrasonic scratching (Fig.1a), diamond powder manual scratching (Fig.1b), and scalpel scratching (Fig.1c), and on untreated mirror polished Si(111) substrate (Fig.1d). Grain size of the diamond films is about 1 μm in Fig.1a, which is common for CVD diamond films, 0.5-3 μm in Fig.1b, and about 3 μm in Fig.1c. In Fig.1d, the diamond grains are the largest of all the films, while the nucleation density is the lowest and only separated diamond particles can be observed.

To understand the substrate effects on quality of the diamond films, XRD measurements were done on the four diamond films (Fig.2, with the same sequence as above mentioned). XRD patterns of all the films exhibit diamond peaks at 43.93°, 75.29°, and 91.49°, assigned respectively to diffraction peaks of (111), (220) and (311) diamond crystalline planes [13]. Silicon carbide peaks cannot be seen in all the XRD patterns but Fig.2c, indicating that silicon carbide can be produced at the defect sites generated by the scalpel scratching. The intensity ratios of I (111) / I (220) of the diamond films are 15.1 (Patterns a), 6.4 (Patterns b), 5.2 (Patterns c) and 5.0 (Patterns d), which are larger than typical value (around 4) for a randomly oriented diamond film. The film deposited on silicon substrate treated by diamond powder ultrasonic scratching shows the highest (111)-textured growth.

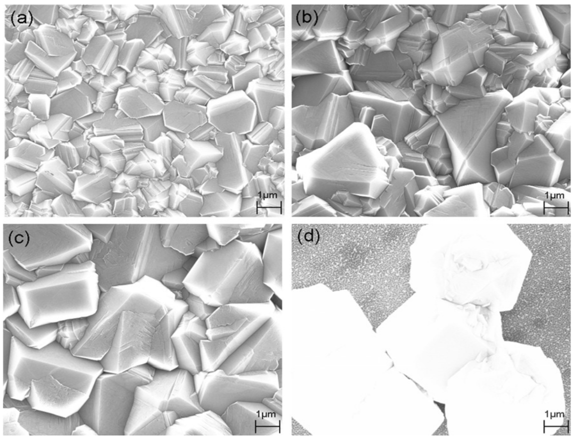

Fig.1 SEM images of diamond films grown 8 h on Si(111) substrates treated by a) diamond powder ultrasonic scratching b) diamond powder manual scratching and c) scalpel scratching and d) on untreated mirror polished Si(111) substrate.

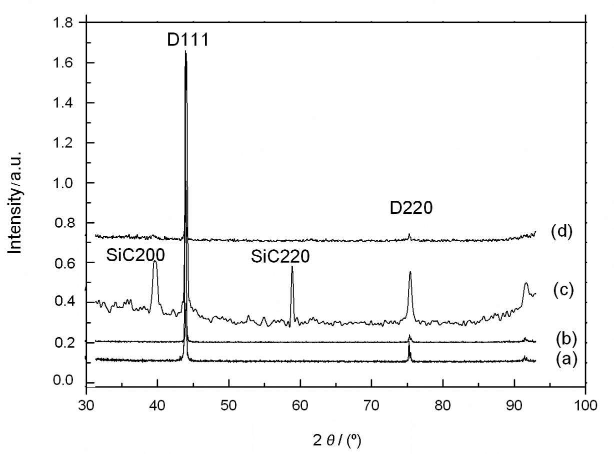

Fig.2 XRD patterns of diamond films grown for 8 h on Si(111) substrates scratched by diamond powder ultrasonically (a) or manually (b), by scalpel (c), and on untreated mirror polished Si(111) substrate (d).

To investigate the effects of defects on diamond nucleation, diamond films were deposited on the four kinds of substrates with just the first 15 min gas flows at flow rates of 4 and 100 SCCM for CH_4 and H_2, respectively. SEM images of the films are shown in Fig.3. For comparison, SEM images of the films grown on the four kinds of substrates for 15 min gas flow at flow rate of 4 and 100 SCCM for CH_4 and H_2 respectively and then 1 h gas flow at 1 and 100 SCCM for CH_4 and H_2, are shown in Fig.4.

Fig.3a and Fig.3b show diamond particles of 10~150 nm and 50~150 nm in size, which are adhered to small carbon particles on the substrate. In Fig.3c, diamond particles (~100 nm) grown on nanowire-like structures can be seen clearly. In Fig.3d, no diamond but carbon nanoparticles were grown on the untreated mirror polished silicon substrate.

As shown in Fig.4a, coalesced diamond film was grown on silicon substrate scratched ultrasonically with diamond powder. Fig.4b and Fig.4c show the coalescing diamond particles adhered on the substrates. In Fig.4d, only small amount of diamond particles grew on carbon nanoparticles. SEM images of the four substrates (not shown here) revealed that there were nano-sized damages (5-10 nm) on the silicon substrate of diamond powder ultrasonic scratching, micro-sized damages (~1 μm) on the silicon substrate of diamond powder manual scratching, defects of 100-200 nm on the scalpel-scratched silicon substrate, and few defects on the untreated silicon substrate.

The diamond nucleation density is the highest on the silicon substrate scratched ultrasonically with diamond powder, while it is the lowest on the untreated silicon substrate. This is related to difference in defect density and structure of the substrates. There are a large number of nano-sized defects (5-10 nm, not shown here) on the substrate of diamond powder ultrasonic scratching, but few defects on the untreated substrate. It has been shown that nano-sized defects induced by ultrasonic scratching could enhance the diamond nucleation and increase the nucleation density. The high diamond nucleation density on silicon substrate ultrasonically scratched with diamond powders is in agreement with the results of Hao *et al*[14]. The density of crystalline diamond nanoparticles was estimated at about 10^7 cm^{-2}, therefore nano-damaged sites on the surface are the main active sites for the diamond nucleation.

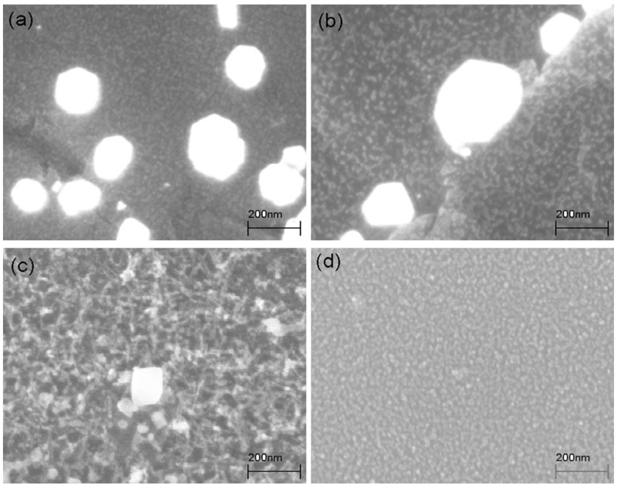

Fig.3 SEM images of the diamond films grown for 15 min on Si(111) substrates treated by a) diamond powder ultrasonic scratching, b) diamond powder manual scratching and c) scalpel scratching, and d) on untreated mirror-like polished Si(111) substrate.

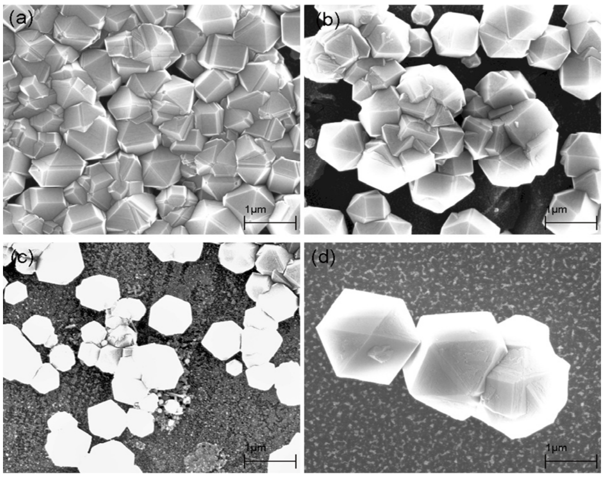

Fig.4 SEM images of diamond films deposited for 15 min gas flow in flow rate of 4 and 100 SCCM for CH_4 and H_2 respectively and then 1 h gas flow in flow rate of 1 and 100 SCCM for CH_4 and H_2 on silicon substrates by a) diamond powder ultrasonic scratching, b) diamond powder manual scratching, and c) scalpel scratching, and d) on untreated mirror polished silicon substrate.

In some way, the four film samples differ in just the method of substrate treatment, hence different nucleation densities. The highest nucleation density on ultrasonically scratched substrate causes highly (111)-textured diamond film. Although the scalpel scratched substrate had defects of 100-200 nm in size (much larger than that the diamond powder scratched substrate) and grew diamond film with larger grain size and lower nucleation density (Fig.1), it provided an environment for diamond growth freely without the interference from nearby crystallites and the diamond crystallites kept their facets during growth. Depending on the defect geometry of differently treated substrates, diamond could nucleate with dot-like morphology on the silicon substrates of diamond powder scratching, or with wire-like morphology on the scalpel scratched substrate.

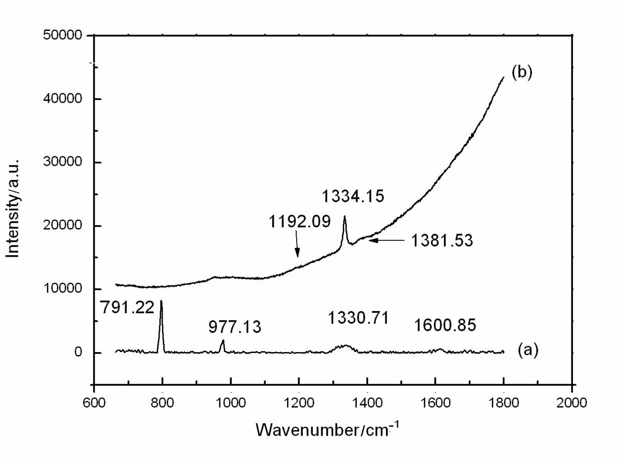

Fig.5 Raman spectra of the diamond films, deposited a) for 15 min and b) for 8 h on scalpel scratched silicon substrate.

Fig.5 shows Raman spectra of the diamond films grown for 15 min (Spectrum a) and 8 h (Spectrum b) on silicon substrates of scalpel scratching. The films correspond to the nucleation stage and prolonged growth stage, respectively. Spectrum a has two broad bands: the "D" band for disordered carbon at about 1330 cm^{-1}, and "G" band for graphite at approximately 1600 cm^{-1}[15]. Raman scattering is 50-60 times higher for sp^2-bonded carbon compared to sp^3-bonded carbon, hence the dominating diamond component and small amount of graphitic carbon in the film[16]. Spectrum a) also contains two bands centered at 790 and 970 cm^{-1}, which are the characteristic peaks for the transverse (TO) and longitudinal (LO) optical modes of silicon carbide[17]. The sharp peak at 1334 cm^{-1} in Spectrum b) is the signature of diamond, confirming that the film with facet structure (Fig.1c) is diamond. The 2 cm^{-1} shift to a higher wave number indicates a compressive residual stress on the specimen. Johnston *et al*[18] demonstrated that the Raman band of diamond moved to higher wave number shifts with increasing pressure applied. It could be supposed that the stress was originated from the defects introduced by scratching. Amorphous carbon produces a broad asymmetric hump in the 1000-1600 cm^{-1} region. Both graphite and amorphous carbon have Raman scattering efficiencies greater than that of diamond. This means that for identical numbers of sampled atoms in the three carbon forms, i.e. diamond, graphite and amorphous carbon, the graphite and amorphous carbon samples would give a much larger Raman signal than the diamond sample. This shows that high purity diamond film was formed under conditions of the experiment. Besides, one also sees three broad peaks centered at 970 cm^{-1}, 1190 cm^{-1} and 1380 cm^{-1}. The 970 cm^{-1} peak was the second-order features of silicon[19]. The peak at 1190 cm^{-1} indicates the presence of nanocrystalline diamond[20]. The small peak around 1380 cm^{-1} is presumably related to symmetric C–H deformational vibrations of sp^3 CH_3 groups[21].

Based on the above observations, it can be speculated that diamond nucleation depends on the structure of defects. Highly (111)-textured diamond film of high nucleation density was deposited on the silicon substrate with nano-sized defects created by diamond powder ultrasonic scratching. The nano-sized defects created by ultrasonic scratching can promote diamond nucleation. The scalpel scratched silicon substrate had larger size defects, on which a β-SiC nanowire layer forms for diamond nucleation on the β-SiC nanowire layer. The specially structured β-SiC layer reduces crystal lattice mismatch between silicon and diamond, and its formation is essential for the alignment of diamond growth[22,23]. In our experiment, the substrate serves as Si source for the SiC formation with Si atoms diffusing to the surface layer[24], and the metallic particles from the scalpel scratching catalyzes the formation of SiC[25]. Obviously, it is easier for Si atoms to diffuse out at the defect sites. The C diffusion into surface layer of Si was also observed by Sun *et al*[26]. The β-SiC nanowire formation under the experimental condition is consistent with the results of Kim *et al*[27].

4 Conclusion

Effects of different defects on diamond nucleation and textured growth were investigated experimentally. Highly (111)-textured diamond film can be deposited on Si (111) substrate scratched ultrasonically by diamond powder, which create nano-sized defects during the scratching. The nano-sized defects cause high density diamond nucleation and coalescence of individual particles during the film growth. High quality (111)-textured diamond films can be prepared with prolonged growth. Different defect structures affect the diamond nucleation. The nano-sized defects created by the ultrasonic scratching can promote diamond nucleation without the formation of silicon carbide interlayer, but the formation of silicon carbide nanowire layer is essential for the nucleation of diamond on the scalpel scratched silicon substrate.

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