Low-pressure microwave plasma nucleation and deposition of diamond films

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Abstract

Low-pressure microwave plasma nucleation and deposition of diamond films were investigated in the pressure range 10 mTorr to 10 Torr, at low substrate temperatures of 400–750 °C, using high methane concentration of 2%–15% and oxygen concentrations of 2%–10% in hydrogen plasmas. Diamond film deposition was performed in a microwave plasma system consisting of a microwave plasma chamber, a downstream deposition chamber and an r.f. induction heated sample stage. The deposition system can be operated in either localized microwave plasmas or extended electron cyclotron resonance (ECR) plasmas by varying the sample stage position. Initial nucleation for diamond growth was achieved by ECR plasmas under a low pressure of 13 mTorr and at 600 °C. Diamond nucleation on BN and SiC interlayer materials was demonstrated by depositing well faceted diamond crystallites onto amorphous BN and cubic SiC coated silicon substrates. Low-pressure ECR microwave plasma deposition and the use of BN and SiC as interlayer materials for coating substrates are new practical methods for generating diamond nuclei to promote diamond film growth on non-diamond surfaces. Cathodoluminescence (CL) studies on diamond films deposited at 10 Torr pressure show that CL emissions at 430, 530, 560 and 740 nm can be employed to characterize the quality of diamond films. Scanning electron microscopy (SEM) of diamond films deposited at 600 °C with 5% CH_4 and 5% O_2 in H_2 plasmas has shown high-quality well faceted crystallites of 1/2 μm sizes. CL measurements on these diamond films show very few nitrogen impurities and no detectable silicon impurities.

1. Introduction

The discovery of chemical vapor deposition (CVD) of diamond films has made available a practical form of diamond for technological applications. However, diamond film deposition still has various limitations; one of the major challenges in diamond film growth is to nucleate diamond on non-diamond surfaces. In fact, a standard method to prepare silicon substrates for diamond film deposition is to scratch the silicon surface with diamond powder to produce nucleation sites for diamond growth. This nucleation method is highly undesirable for diamond film applications since it perturbs the application surface. Hence, new nucleation methods, which do not perturb the diamond film growth surface, are much needed for developing a viable diamond film technology.

Microwave plasma-enhanced CVD of diamond films has been established as one of the standard methods for producing high-quality polycrystalline diamond films [1–4]. Microwave plasma depositions of diamond films are generally performed at high pressures of 50–100 Torr, high temperatures of 850–950 °C and low methane concentrations of less than 1% in H_2 plasmas. Microwave plasmas under such high pressures are con-

fined to a localized, ball-shaped region, which has a limited deposition area. Technological applications of diamond films in optics, electronics and protective coatings require large-area, uniform films deposited at low temperatures. Extended microwave plasmas can be obtained under low pressures to increase the deposition area of diamond films. Hiraki *et al.* [5] reported diamond film depositions using extended magnetomicrowave plasmas at a low pressure of 0.1 Torr. The increase in methane concentration in the plasma and the addition of oxygen to the plasma can be employed to lower the deposition temperature of diamond films [6, 7].

In this paper, we report diamond nucleation and deposition using low-pressure microwave plasmas and coating the silicon substrate with interlayer materials, such as boron nitride (BN) and silicon carbide (SiC). Diamond film depositions were investigated in the low pressure range of 10 mTorr to 10 Torr, at low substrate temperatures of 400–750 °C, using high methane concentrations of 2%–15% and oxygen concentrations of 2%–10% in hydrogen plasmas. The cathodoluminescence (CL) spectroscopy of diamond films deposited at 10 Torr was studied. Scanning electron microscopy (SEM) and Raman spectroscopy were employed to characterize films deposited under various conditions.

2. Experimental techniques

Diamond film depositions were performed in a microwave plasma deposition system using gas mixtures of H_2, CH_4 and O_2. The deposition system consists of a microwave plasma chamber, a downstream deposition chamber and an r.f. induction heated sample stage. The microwave plasma source and the induction heated sample stage were manufactured by Applied Science and Technology, Inc. Figure 1 shows a schematic diagram of the microwave plasma deposition system. The sample stage can be located at a distance of 5 inches below to 12 inches above the aperture of the plasma chamber. The deposition system can be operated in either localized microwave plasmas or electron cyclotron resonance (ECR) extended microwave plasmas by locating the sample stage at an appropriate position. The substrate is independently heated by r.f. induction using a 3.75 kW, 60 kHz power supply. Diamond film deposition conditions were investigated in the pressure range 10 mTorr to 10 Torr, at substrate temperatures of 400–750 °C, using CH_4 concentrations of 2%–15% and O_2 concentrations of 2%–10% in hydrogen plasmas.

Diamond growth was performed on bare silicon wafers and silicon coated with interlayers of SiC or BN grown by plasma-assisted CVD. The bare silicon was pretreated ultrasonically in a methanol solution suspended with 10 μm size diamond particles for approximately 10 min prior to diamond growth. However, diamond growth obtained on the interlayers was accomplished without diamond abrasion of the growth surface.

The microwave plasma deposited diamond films were characterized by SEM, Raman and CL spectroscopy.
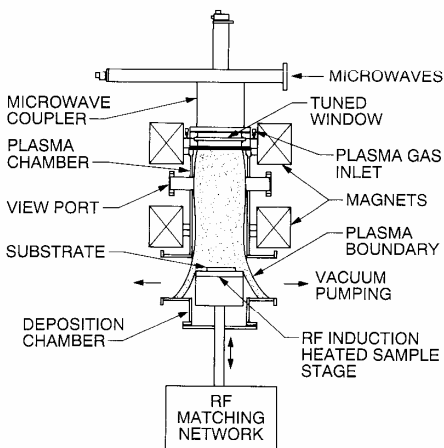

Fig. 1. Schematic diagram of the microwave plasma deposition system.

The CL spectra of diamond films were systematically investigated as a function of the deposition conditions, and the film morphology was examined by SEM. CL measurements were performed with a JEOL 840-F field emission scanning electron microscope. The CL optical collection system and cryogenic specimen stage were designed and constructed at the Jet Propulsion Laboratory [8]. The luminescence emitted from the sample was collected with an ellipsoidal mirror which focuses the radiation onto a coherent optical fiber bundle leading outside the SEM vacuum chamber to a 0.25 m focal length monochromator. The coherency of the bundle allows for direct imaging of light at the second ellipsoidal focus into the entrance slit of the monochromator. The slit width of the monochromator was chosen to give a spectral resolution of 6 nm. An electron beam current of 600 pA (rastered over a 120 μm × 90 μm region for the CL spectra) at an accelerating voltage of 20 kV was used to probe the diamond film sample which was maintained at a temperature of about 77 K.

3. Results and discussion

Low-pressure microwave plasma nucleation and deposition of diamond films were investigated in the pressure range 10 mTorr to 10 Torr and in the temperature range 400–750 °C. The substrate is independently heated by r.f. power and the substrate temperature is monitored and controlled by a thermocouple embedded in the graphite susceptor of the RF induction heater. The sample stage is located at a position such that the microwave plasma is not in direct contact with the substrate surface during the growth of the diamond film. Therefore, the microwave plasma is not contributing significantly to the substrate heating, owing to the low deposition pressure, the low microwave power and the sample stage location. The substrate surface temperature for the diamond growth is estimated to be lower than the substrate temperature measured at the graphite susceptor since there is likely to be a thermal gradient between the substrate and the heat source. However, as reported in the literature [7], direct microwave plasma heating of the substrate is often employed in diamond film deposition. In the case of the direct plasma heating, the substrate surface temperature is generally higher than the measured substrate temperature.

Diamond nucleation on silicon substrates has been investigated using low-pressure ECR microwave plasmas and by coating the silicon substrate with interlayer materials, such as BN and SiC. Initial nucleation for diamond film growth on silicon substrates has been demonstrated at a pressure of 13 mTorr and a substrate temperature of 600 °C using an ECR plasma containing
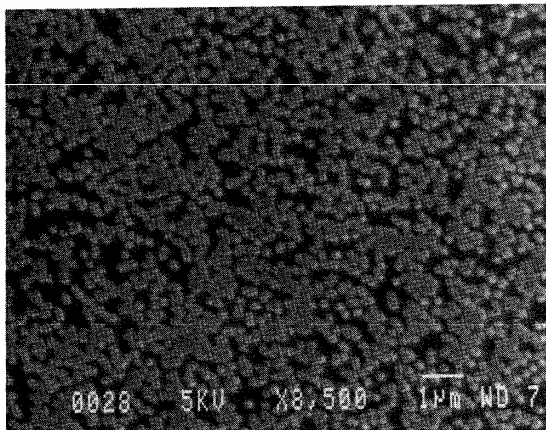
Fig. 2. SEM image showing initial nucleation of diamond growth at 13 mTorr and 600 °C with 15% CH_4 and 10% O_2 in H_2 plasmas.
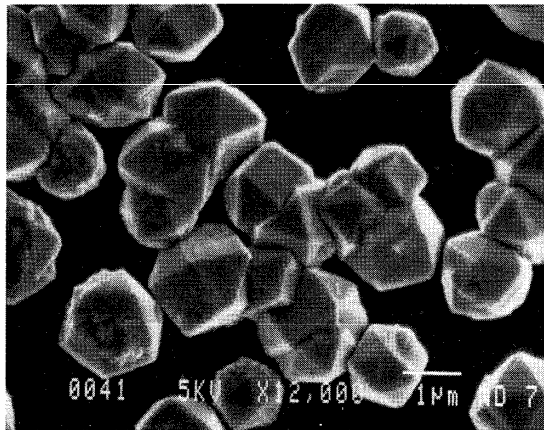

Fig. 3. SEM image showing diamond crystallites deposited onto an SiC coated silicon substrate at 10 Torr and 750 °C with 2% CH_4 and 5% O_2 in H_2 plasmas.

15% CH_4 and 10% O_2 in H_2. Figure 2 shows a SEM image demonstrating the initial growth of ball-shaped diamond microcrystallites with sizes of about 0.2 μm. These microcrystallites indicate that the microwave plasma deposition of diamond films may be achieved at a pressure as low as 10 mTorr using the ECR plasma conditions.

Amorphous boron nitride (a-BN) films were deposited onto silicon substrates using B_2H_6 and N_2 mixed gas ECR plasmas under a pressure of 0.3 mTorr and at a substrate temperature of 600 °C. Silicon substrates coated with approximately 0.1 μm of cubic SiC were obtained from the Kyoto Institute of Technology. The cubic SiC films were deposited by plasma-assisted CVD using Si_2H_6 and C_2H_2 as source gases at a substrate temperature of 800–1150 °C [9]. High-quality diamond crystallites were deposited onto both a-BN and cubic SiC coated silicon substrates under a pressure of 10 Torr and at a substrate temperature of 600–750 °C. The surface of the interlayer was not subject to diamond abrasion prior to diamond growth. Figure 3 shows well faceted diamond crystallites on cubic SiC coated silicon substrates; equally well faceted diamond crystallites were also observed on a-BN coated silicon substrates. The nucleation rate for diamond growth on the interlayers was found to be approximately 0.1 μm h⁻¹. These results demonstrate the feasibility of employing BN and SiC as interlayer materials for diamond growth.

Figure 4 shows a CL spectrum of diamond films deposited at a substrate temperature of 700 °C. The microwave plasmas for the deposition of these films are generated from a gas mixture of 5% CH_4 and 5% O_2 in H_2 under a pressure of 10 Torr using a microwave power of 550 W. The CL spectrum shown in Fig. 4 has
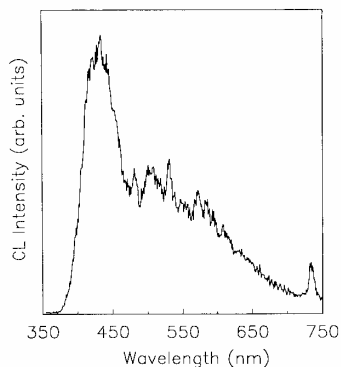

Fig. 4. CL spectrum of a diamond film deposited at 10 Torr and 700 °C with 5% CH_4 and 5% O_2 in H_2 plasmas.

a dominant emission at 430 nm and several weak emissions occurring at 480, 500, 530, 560 and 740 nm. The main CL peak at 430 nm is a characteristic line of diamond which has been labeled as "band A" and is attributed to the nearest neighbor donor–acceptor recombination [10, 11]. The group of weak CL peaks between 500 and 600 nm is associated with the nitrogen-vacancy complexes [12]. The single, weak CL peak at 740 nm is identified with interstitial silicon impurities [13].

Systematic investigations of the CL spectra of diamond films show that the CL of the diamond band A, centered at about 430 nm, can be employed as a sensitive method for identifying the quality of the diamond film. The CL intensities of diamond films deposited at substrate temperatures of 400–750 °C were measured at 430, 530 and 560 nm respectively, under the same
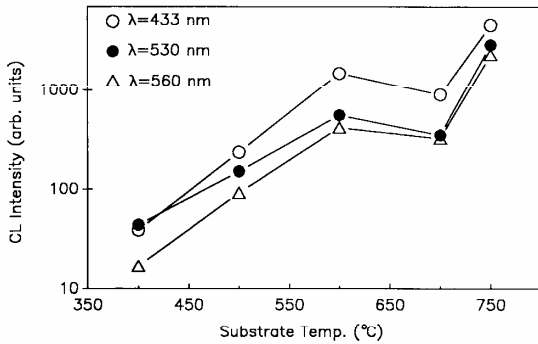
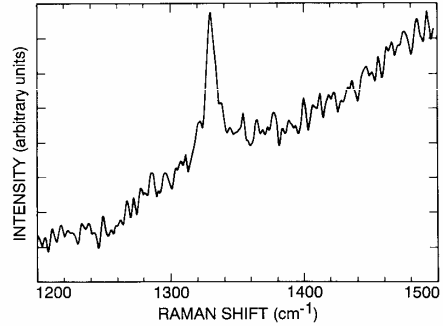Fig. 5. CL intensities of diamond films as a function of substrate temperature.

Fig. 6. Raman spectrum of a diamond film deposited at 10 Torr and 650 °C with 5% CH_4 and 2% O_2 in H_2 plasmas.

Fig. 7. Raman spectrum of a diamond film deposited at 10 Torr and 700 °C with 5% CH_4 and 5% O_x in H_2 plasmas.

experimental conditions. The CL intensities measured under such a controlled condition are compared to show the relative variation of film quality. Figure 5 shows the CL intensities of diamond films as a function of substrate temperature. The intensity of the main diamond CL line at 430 nm increases with the substrate temperature, indicating a higher quality for diamond films deposited at high temperatures of 600–750 °C. The weak CL lines at 530, 560 and 740 nm, which are related to the nitrogen and silicon impurities and vacancy complexes in diamond films, also show an increase in CL intensity with substrate temperature. The increase in impurity-related CL intensities may indicate that the impurity incorporation into the diamond film is activated at high temperatures. Figure 5 shows that the quality of diamond films as measured by the CL intensities is optimized at a substrate temperature of about 600 °C. CL intensity measurements indicate that diamond films deposited at 600 °C have shown very few nitrogen impurities and no detectable silicon impurities.

In addition to the CL spectroscopy, we also performed Raman spectroscopy, SEM and CL imaging to characterize low-pressure microwave plasma deposited diamond films. These diamond films are optically transparent in the visible spectrum since colored interference fringes have been observed in these films. A typical Raman spectrum of a diamond film, deposited at 10 Torr pressure and 650 °C substrate temperature using a microwave plasma containing 5% CH_4 and 2% O_2 in H_2, is shown in Fig. 6. The diamond Raman line at 1332 cm^{-1} is clearly observed and there is a detectable background which can be associated with non-diamond carbon. Figure 7 shows the Raman spectrum of another diamond film deposited at 10 Torr and 700 °C with 5% CH_4 and 5% O_2 in H_2 plasmas. This Raman spectrum consists of three components which can be identified as
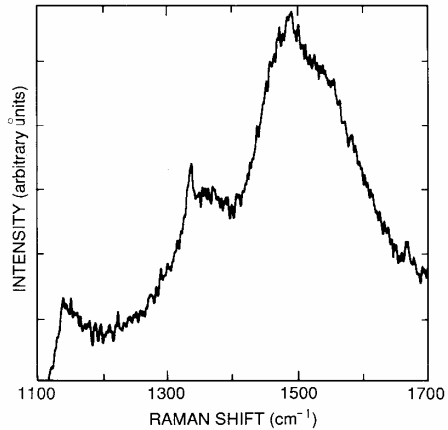
a broad peak of amorphous diamond-like carbon [14–16] centered at 1500 cm^{-1}, a characteristic diamond line at 1332 cm^{-1}, and a weak line at 1140 cm^{-1} of nanocrystalline diamond particles [17]. By increasing the oxygen concentration to 5% and the substrate temperature to 700 °C, the Raman lines of this diamond film indicate that amorphous diamond-like carbon and nanocrystalline diamond components in the film are increased.

A SEM image and a CL image of a diamond film deposited at 600 °C are shown in Figs. 8 and 9 respectively. The CL image of the diamond film is formed by monitoring the CL emission at 435 nm. The SEM image shows that the diamond crystallites are well faceted with dominant (100) faces and the size of the crystallites is about 1/2 μm. The bright spots in the CL image can be identified as the CL emissions from the (100) faces of the diamond crystallites.
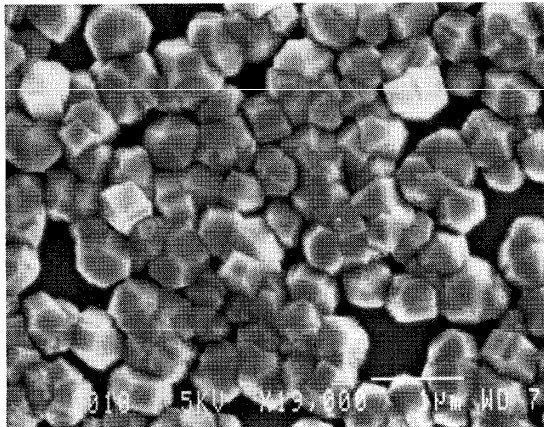
Fig. 8. SEM image of a diamond film deposited at 10 Torr and 600 °C with 5% CH_4 and 5% O_2 in H_2 plasmas.
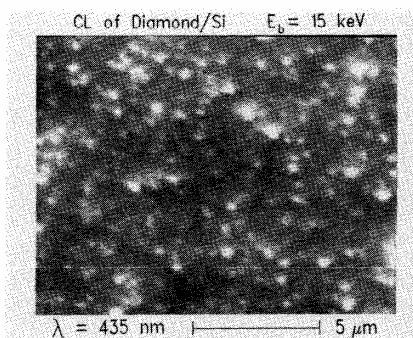

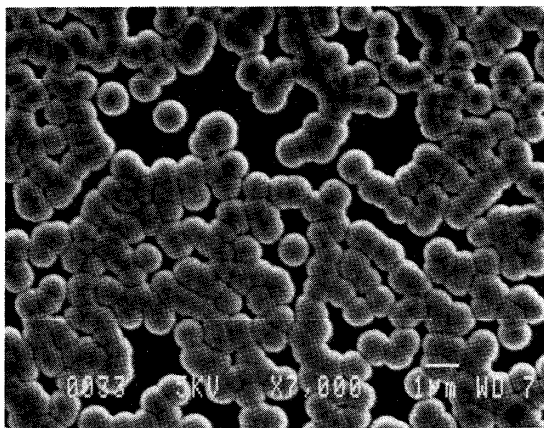Fig. 9. CL image of the same diamond film shown in Fig. 8.

Fig. 10. SEM image showing ball-shaped crystallites of a film deposited at 10 Torr and 700 °C with 15% CH_4 and 10% O_2 in H_2 plasmas.

The microwave plasma deposition parameter space of diamond films was expanded by increasing the methane concentration in the plasma and by lowering the deposition pressure. Figure 10 shows a SEM image of a film deposited with 15% CH_4 and 10% O_2 in H_2 at a pressure of 10 Torr and at a substrate temperature of 700 °C. The crystallites in this film have a ball-shaped morphology. XRD of this film has shown some weak diamond diffraction patterns, but there is no detectable CL spectrum owing to the lack of well developed diamond (100) faces. This film is also optically transparent as are those diamond films deposited with lower methane concentrations.

4. Conclusions

Low-pressure microwave plasma nucleation and deposition of diamond films were investigated in the pressure range 10 mTorr to 10 Torr, at low substrate temperatures of 400–750 °C, using high methane concentrations of 2%–15% and oxygen concentrations of 2%–10% in hydrogen plasmas. Initial nucleation for diamond growth was achieved by ECR plasmas under a low pressure of 13 mTorr and at 600 °C. Diamond nucleation on BN and SiC interlayer materials was demonstrated by depositing well faceted diamond crystallites onto a-BN and cubic SiC coated silicon substrates. Low-pressure ECR microwave plasma deposition and the use of BN and SiC as interlayer materials for coating substrates are new practical methods for generating diamond nuclei to promote diamond film growth on non-diamond surfaces. Cathodoluminescence (CL) spectroscopy was demonstrated to be a useful microoptical characterization technique for diamond films. CL spectroscopy was employed to determine the quality of microwave plasma deposited diamond films. High-quality, well faceted diamond films were deposited at 10 Torr and 600 °C using 5% CH_4 and 5% O_2 in H_2 plasmas; CL measurements on these films show very few nitrogen impurities and no detectable silicon impurities.

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