

Electrical properties of diamond films grown at low temperature

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Abstract

The unique electronic properties of diamond, associated with the emergence of chemical vapour deposition (CVD) methods for the growth of thin films on non-diamond substrates, have led to considerable interest in electronic devices fabricated from this material. In our previous work, we found that polycrystalline diamond films can be deposited at 250 °C using CH₄–CO₂ gas mixtures. Studying the electrical properties and the upcoming problems of applications of low-temperature diamond films are relevant concerns.

In this work, the electrical properties of diamond films grown at low temperatures were studied and compared with those of conventional diamond films. Platinum was used as the upper electrode. The resistivity of low-temperature diamond was around three orders of magnitude lower than that of conventional diamond. However, both the low temperature and conventional growth diamond exhibited rectifying behavior when platinum was used as the upper electrode.

Keywords: Diamond; Electrical properties and measurements

1. Introduction

Since it was discovered that diamond films could be synthesized in a low pressure and low temperature chemical vapor deposition (CVD) process, a large number of different CVD methods have been used to make low-temperature deposition diamond films, e.g., hot-filament chemical vapor deposition (CVD), microwave plasma CVD, and microwave electron cyclotron resonance discharge [1–3]. Consequently, the electrical properties of semiconductive diamond films have received extensive attention [4,5]. Diamond films are normally synthesized from gas mixtures that include a small amount of hydrocarbons in hydrogen; in addition, the typical growth temperatures range from 700 to 1000 °C [6,7]. Growing diamond films at low temperatures (less than 500 °C) is necessary for many applications since many substrate materials, e.g. GaAs, plastics, ZnS, and MgF₂, are unstable at higher temperatures. Diamond films are relatively new materials and will be extensively adopted for next century VLSI applications. However, the electrical properties of low temperature deposition diamond films have not been investigated despite the fact that numerous studies of the detailed electrical properties of diamond films have been conducted.

Our previous studies [8,9] have demonstrated that diamond films could be deposited without adding extra hydrogen gas to the hydrocarbons feed with a higher growth rate and improved crystallinity resulting from using CH₄–CO₂ gas

mixtures. More specifically, the CH₄–CO₂ gas mixtures are suitable for low-temperature diamond growth [10,11].

Therefore, in this work, not only are low temperature (250 °C) diamond films investigated by microwave plasma chemical vapor deposition (CVD) but a comparison is made with the sample obtained at a higher temperature (850 °C) diamond film.

2. Experimental details

Polycrystalline thin diamond films were prepared by microwave-assisted plasma-enhanced chemical vapor deposition (PECVD) on (100) p-type silicon. The microwave power was power set at 450 and 290 W, and the reaction periods were 3 and 24 h for high-temperature and low-temperature diamond film growth, respectively. The base pressure was maintained below 0.01 Torr in all cases. In order to grow a continuous film, the substrate was scratched using diamond powders (particle size of 1–2 μm).

Low temperature deposition was achieved by not only cooling the substrate holder with a water cooling system but also by decreasing both the gas pressure and the microwave output power as compared with conventional high-temperature deposition conditions. Therefore, the values for the temperature shown in this work are the actual substrate surface temperature. The total pressure was adjusted from 25 to

Table 1
Experimental conditions and the selected properties of diamond films

No.	Gas flow rate of CO ₂ (= 30 sccm)		Reaction pressure (Torr)	Substrate temperature (°C)	P-Si(100) substrate	
	Gas flow rate of CH ₄ (sccm)	Microwave power (W)			Reverse saturation current (nA)	Breakdown voltage (V)
H182	18.2	450	25	850	400	94
L550	17.5	290	25	550	650	54
L250	16.1	290	6	250	780	45

6 Torr when the microwave output power was fixed at 290 W. For high quality diamond deposition, both the substrate temperature and the volume ratios of [CH₄]/[CO₂] (in volume percent) were changed from 550 to 250 °C and 58.1 to 50.1%, respectively.

SEM was then used to observe the morphology of the films. The crystallinity and quality of the films were determined by Raman spectroscopy. In the Raman experiment, an Ar laser (514.5 nm) with an output power of 200 mW was used.

Next, the platinum electrodes fabricated by conventional photolithography procedure were deposited on the diamond films. The films thickness of the deposited Pt was approximated to be 2000 Å. A lift-off method was also employed to reach the final pattern consisting of a circular-dot pattern on diamond films with a diameter of 100 µm. The reasons for adapting Pt as the contact materials in this study are: (a) Pt is inert in air and therefore should have a natural heat stability, (b) Pt is more adhesive than other metal contacts, and (c) Pt yields the minimum contact resistivity of the metals.

The experimental conditions are listed in Table 1. The scratched Si substrates were then dipped into a solution of HF:H₂O = 1:100 for a few seconds to remove the native oxide of the silicon. Next, any non-diamond surface layer was attempted to be removed by cleaning the diamond films in a saturated solution of CrO₃ in H₂SO₄ at 170 °C for 10 min. This was followed by rinsing in a 1:1 boiling solution of H₂O₂ and NH₄OH. The diamond films were then thoroughly cleaned with deionised (DI) water and dried with a jet of nitrogen gas. Conventional photolithography was used to pattern thin photoresist in a positive mask of circles of various sizes ($\approx 7.5 \times 10^{-4}$ cm²) on the surface of the diamond films. The patterned samples were hardbaked at 140 °C for 30 min.

An HP-4145B semiconductor parameter analyzer was used to measure the current–voltage (I–V) characteristics of the platinum–diamond contacts. The applied voltage for each experiment was varied from –100 to 100 V.

The infrared absorption characteristics of diamond films were studied using a Nicolet 510 FTIR spectrometer with a Michelson-type interferometer. Infrared data were taken with a resolution of 2 cm⁻¹ over the range from 3400 to 2400 cm⁻¹. Free-standing diamond films were produced by growing on Si(100) substrate by the dissolution of the silicon using a mixture of HF and HNO₃ acids (3:1) diluted by about 50% of DI water. Infrared spectra recorded by using pellets

of free-standing diamond films compressed with KBr provide improved resolution.

3. Results and discussion

The selected properties of diamond films studied in this work are presented in Table 1. The film labeled H182 is deposited at a high (850 °C) deposition temperature and the methane flow rate of 18.2 sccm is used. The films labeled L550 and L250 were obtained using low temperature deposition conditions. All of the films were deposited using a CO₂ flow of 30 sccm and various CH₄ flows to obtain good quality diamond films.

3.1. Morphology and Raman spectroscopy of three different deposition diamond films

The underlying mechanism of diamond nucleation and growth remains somewhat unclear. A few parameters such as the growth temperature and the methane/carbon dioxide ratio in the reaction gas mixture can generally affect the growth of diamond films. Results obtained in our previous study [12] suggest that an oxygen addition would subsequently lead to the formation of sufficient gas phase OH to remove nondiamond carbon from the films. Therefore, our results show that, at low temperature conditions, diamond films can be deposited using a lower CH₄ concentration than that required for conventional high temperature deposition. Furthermore, the oxygen atoms directly decomposed from CO₂ play a critical role in low temperature diamond growth. Fig. 1(a) shows the surface morphology, which was deposited using [CH₄]/[CO₂] under 69%, microwave power of 450 W, total gas pressure of 25 Torr, deposition time of 3 h, and a growth substrate temperature of 850 °C. The deposition of good crystallinity films were observed by SEM. The morphology of the film possessed (111) facets and consisted of crystallinities with 3–5 µm in size. In order to obtain low-temperature diamond film, the microwave power was decreased to 290 W as a first step. The low-temperature diamond films were achieved by decreasing both the gas pressure and the microwave output power from the conventional high-temperature deposition conditions. The surface topographies of diamond films at 550 and 250 °C are shown in Fig. 1(b) and (c). The film shown in Fig. 1(b) consisted of crystallites that are 0.5–

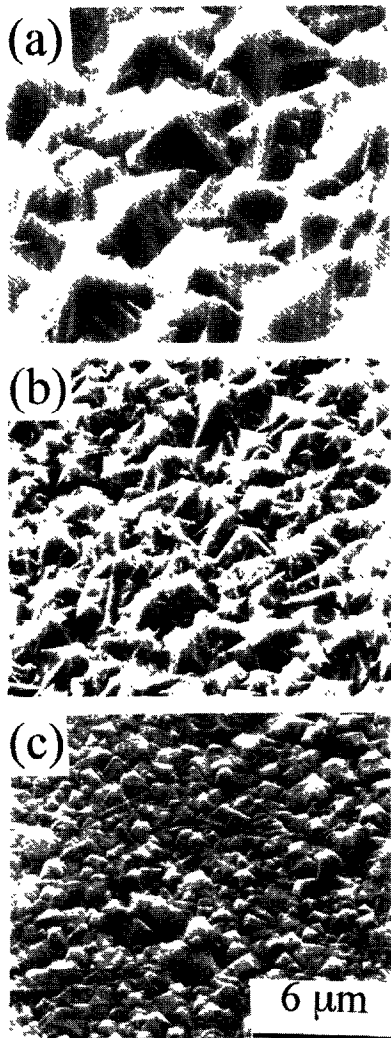


Fig. 1. Scanning electron micrographs of diamond films deposited under various conditions: (a) sample H182, $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 18.2$ sccm, deposition temperature 850°C ; (b) sample L550, $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 17.5$ sccm, deposition temperature 550°C ; (c) sample L250, $\text{CO}_2 = 30$ sccm, $\text{CH}_4 = 16.1$ sccm, deposition temperature 250°C .

$2\ \mu\text{m}$ in size. Lowering the total pressure and substrate temperature, as shown in Fig. 1(c), would also increase the nucleation density as well as result in a smaller grain size of about $0.1\text{--}0.5\ \mu\text{m}$.

Fig. 2 shows the Raman signatures for the same samples as Fig. 1. Both of these deposits exhibited peaks (at 1331 and $1329\ \text{cm}^{-1}$, respectively) that correspond to that of natural diamond ($1332\ \text{cm}^{-1}$). The Raman peak shifts exhibited a relationship with the internal stress of the diamond film at low temperature deposition [13]. The deposits formed at 250°C had a broad peak at around $1550\ \text{cm}^{-1}$, characteristic of an amorphous carbon phase with sp^2 bonds. The appearance of this broad peak indicated the presence of disordered carbon, perhaps residing between the diamond grain boundaries.

3.2. I-V characteristics and activation energy calculation

Fig. 3 provides I-V characteristics for the same samples as Fig. 1 with Pt electrodes. Clear rectifying contacts were

obtained. The temperature-dependent I-V characterizations of the point-contact Schottky diode of the intrinsic diamond films were obtained by a semiconductor parameter analyzer (HP 4145B) and a probe station equipped with a heated stage. The sample temperatures were well controlled within 1°C during the measurements. The reverse saturation current and breakdown voltage were about 400 , 650 and $780\ \text{nA}$, and 94 , 54 and $45\ \text{V}$ for the preliminary deposition temperatures of 850 , 550 , and 250°C , respectively. The sample leakage current increased with a decrease in the preliminary deposition temperature. This occurrence was a result of the more enhanced quality and lower defect concentration in the diamond films of the preliminary higher deposition temperature (850°C). However, the breakdown voltage would exhibit an

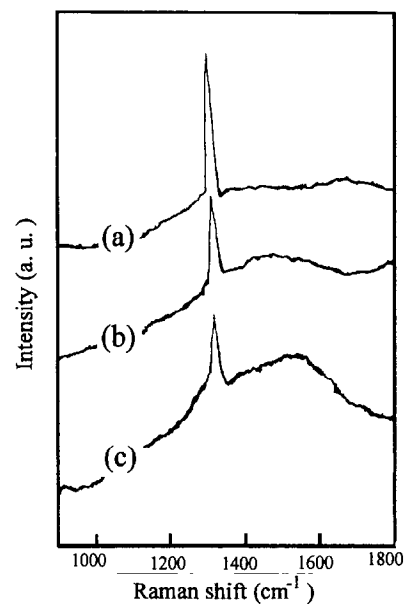


Fig. 2. Raman spectra obtained from the same specimens as Fig. 1.

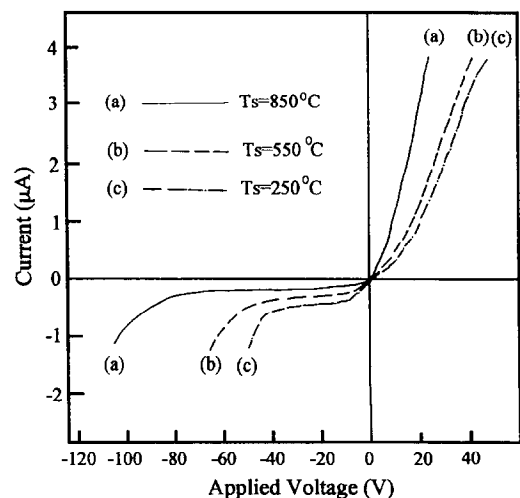


Fig. 3. I-V characteristics of intrinsic diamond films synthesized at the deposition temperature of (a) 850°C , (b) 550°C , and (c) 250°C with Pt electrodes at room temperature.

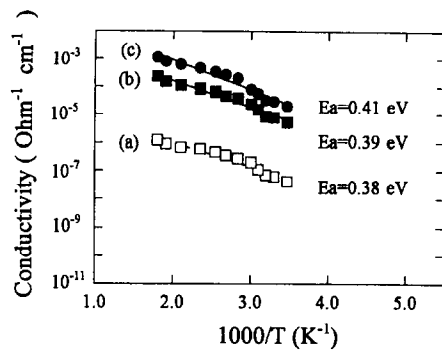


Fig. 4. The temperature dependence of conductivity for intrinsic diamond films synthesized at the deposition temperature of (a) 850 °C, (b) 550 °C, and (c) 250 °C.

opposite behavior. Meanwhile, the forward direction of the I–V curve is the same as that in Fig. 3.

Another feature of these diodes, as observed in Fig. 3, is the gradual rise in current at a low forward bias which is contrary to what is expected for an ideal diode. We believe that a slow rise is to be caused by the series resistance of these diamond films.

The changes in conductivity of polycrystalline diamond films of the above three sample are shown in Fig. 4 as a function of temperature. This figure indicates that the resistivity of low-temperature diamond was around three orders of magnitude lower than that of a conventional diamond. The activation energy extrapolated from the resistivity and the reciprocal temperature are about the same. This indicates that hydrogen atom trapped in the polydiamond dominates the conduction mechanism of diamond. The electrical resistivity of as-deposited plasma chemically vapor deposited (CVD) diamond thin films is usually reported to be in the range of 10^2 – 10^6 Ω cm. This low resistivity of the polycrystalline diamond thin films could be due to hydrogen passivation of defective states [14,15]. According to Landstrass and Ravi [14,15], the resistivity of the as-grown diamond thin films is increased by several orders of magnitude upon annealing at 800 °C in nitrogen gas ambient atmosphere. The effect is assumed by them to be a result of removal of hydrogen from the films or due to a shift in the hydrogen position in the films. This mechanism is corroborated by an observed decrease in resistivity upon hydrogen plasma treatment. Similar effects are observed for a single crystal diamond [15]. Celii et al. [16] correlated the measured electrical resistivity of the microwave plasma deposited polycrystalline diamond thin films with hydrogen content. Albin and Watkins [17] have reported that the electrical properties of diamond thin films can be controlled by hydrogen plasma treatment. Exposure of oxyacetylene-deposited diamond thin films grown on a silicon substrate to a hydrogen plasma resulted in a decrease of several orders of magnitude in its electrical resistivity [18].

Difficulties encountered with low-temperature growth have been clarified as an enhancement of amorphous component production and degradation of crystallinity. Obtaining

a good quality diamond films necessitates a low $[\text{CH}_4]$ for low-temperature growth of diamond films, as stated above. To determine the effect of $[\text{CH}_4]$ on $[\text{H}]$ in the plasma-assisted CVD system, Muranaka et al. [19] adopted plasma emission actinometry using Ar as an actinometer. They found that in the plot of $I_{\text{H}}/I_{\text{Ar}}$ against $[\text{CH}_4]$ in a low output microwave plasma CVD system, $I_{\text{H}}/I_{\text{Ar}}$ was apparently proportional to $[\text{H}]$. Additionally, a steep increase in $I_{\text{H}}/I_{\text{Ar}}$ was clearly observed with a decrease in $[\text{CH}_4]$, implying that a low $[\text{CH}_4]$ provides an excess atomic hydrogen environment. Above results would suggest that the films quality deteriorates below 550 °C. This deterioration may be a result of the incorporation of H atoms from the gas phase into the diamond films [19]. Also, Ravi [20] showed that dissolved hydrogen plays a prominent role in current conduction in these films.

3.3. FTIR analysis of diamond films

FTIR experiments were carried out to examine the difference in bonding behavior of the samples synthesized at various deposition temperatures. Our previous work [19] indicated that dissimilarity occurs in the region of 2400–3400 cm^{-1} due to the C–H vibrational region as shown in Fig. 5. The C–H stretch region (2750–3300 cm^{-1}) contains information about hydrogen bonded to carbon and other atoms, present as impurities, in diamond films. The stretching vibrations of carbon–hydrogen bonds are observed in this region. The dominant absorptions observed in the spectra of the films studied here appears to be near 2850 cm^{-1} and 2920 cm^{-1} and are indicative of symmetric and asymmetric stretching of CH_2 groups, respectively, where the carbon is sp^3 bonded. The spectra in Fig. 5(b) and (c) clearly demonstrate an inequality in absorption intensity for the symmetrical and asymmetrical absorptions of sp^3 bonded CH_2 groups in the diamond films.

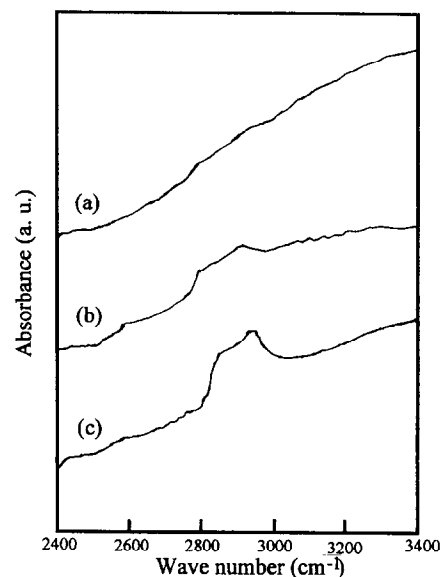


Fig. 5. Infrared absorption spectra of the same specimens as Fig. 1.

4. Conclusion

Diamond films deposited at low temperatures of 550 °C or 250 °C displayed good quality compared with those deposited at high temperature. The results obtained in this study demonstrate that the incorporation of hydrogen in the diamond films has an effect on the electrical properties of actual applications. This effect is a result of the fact that low temperature deposition conditions would increase the nucleation density as well as result in a smaller grain size. The resistivity of low temperature diamond was around three orders of magnitude lower than that of conventional diamond films. Moreover, both the low temperature and conventional growth diamond exhibited rectifying behavior when platinum was used as the upper electrode. This result indicates that the hydrogen trapped in the polydiamond dominates the conduction mechanism of diamond films.

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