FIELD EMISSION FROM NITROGEN-DOPED DIAMOND FILM

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ABSTRACT

Nitrogen-doped diamond films were prepared for the first time using melamine $(C_3H_6N_6)$ as the nitrogen source. To explore the differences in the films produced with different precursors, nitrogen-doped films were also produced using pure nitrogen gas as the source. Since melamine has a ring structure with pre-existing C-N bonds, the incorporation of nitrogen on substitutional sites of diamond lattice are expected. Relatively large amounts of substitutional nitrogen were successfully doped into diamond without degrading its quality. However, when pure nitrogen gas was used as a doping source, the quality of the diamond was not as high as the sample doped with nitrogen by melamine. Raman spectroscopy, photoluminescence spectroscopy (PL), and field emission measurements were carried out to characterize the samples. Nitrogen-doped diamond samples did not exhibit any significant reduction in turn-on fields. It is suggested that nitrogen doping has only a minor effect on the field emission properties of the diamond films.

INTRODUCTION

In diamond, substitutional nitrogen is considered to be a deep level donor whose activation energy is roughly 1.7 eV, while the activation energy of the nitrogen aggregate level is 4.0 eV [1]. The band diagram of diamond with nitrogen impurities are depicted in Figure 1. The activation energy of 1.7 eV is too high to produce useful conduction at room temperature. Even though nitrogen-doped diamond cannot be utilized as an active component of electronic devices, it has been considered as a candidate for field emission applications. It was reported that electron field emission, with low threshold voltages, has been achieved by means of heavy nitrogen doping of diamond [2,3]. Effective field emission from diamond with high concentrations of substitutional nitrogen impurities was successfully demonstrated by Geis *et al.*[2]. Two reasons have been suggested for the field emission enhancement shown in these experiments [4]. First, a sharp potential drop at the depletion layer is produced due to the formation of space charge. Second, since the width of the depletion layer at the metal-diamond Schottky junction can be as little as a few tens of nanometers if doped with 10^{19} Ncm⁻³, electron tunneling from metal to nitrogen-doped diamond region becomes possible. Okano *et al.* [3] achieved the lowest turn-on voltages of ~1.5 V with nitrogen-doped diamond films using urea ((NH₂)₂CO) as a nitrogen source. It was reported that a heavy concentration of nitrogen ($\sim 3.5 \times 10^{20}$ N atoms per cm³) was achieved using this precursor. Pyramidal-shaped nitrogen-doped diamond field emitter were also produced with the same nitrogen source [5]. The turn-on field of this device was 0.2 - 0.3 V/µm, and the emission current exhibited long term stability. Recently, nitrogen-doped nanocrystalline diamond was synthesized by Zhou et al. [6] with $N_{\rm A}/CH_{\rm A}$ plasmas, resulting in nitrogen-doped diamonds with a turn-on field of 3.2 V/µm.

In this research, we have investigated the effect of nitrogen addition on diamond growth. Melamine $(C_3H_6N_6)$ was proposed as a novel nitrogen source for the diamond doping. Since a melamine molecule has a ring structure with pre-existing C-N bonds, it is expected that the nitrogen will be easily incorporated on substitutional sites. The molecular structure of melamine is depicted in Figure 2. The field emission characteristics from these nitrogen-doped diamond films were investigated to view the effects of the substitutional nitrogen.



FIG. 1 Band diagram of diamond with FIG. 2 Molecular structure of melamine nitrogen impurities. [ref 1] $(C_3H_6N_6)$

N

 TABLE 1
 Summary of sample preparation conditions, and resulting properties of the samples.

Sample Number	Substrate	N ₂ conc.	CH₄ conc.	Gas flow rate CH ₄ :H ₂ :N ₂			Depo. time	Raman FWHM	Q _{514.5}	NIF
		(%)	(%)	(SCCM)		(Hrs)	(cm ⁻¹)	(%)		
MP0107	n-type Si	0	0.5	3	597	0	- 4	5	100	0
MP0101	n-type Si	0.5	0.5	3	597	3	4	15	97.26	2.19
MP0103	n-type Si	1	0.5	3	597	6	4	11	96.39	1.62
MP0105	n-type Si	2	0.5	3	597	12	4	10		
MP0122	n-type Si	1	1	3	297	3	6	14	93.99	0.47
MP0093	n-type Si	C ₃ H ₆ N ₆	1	3	297	-	6	6	99.39	15.79
MP0095	n-type Si	C ₃ H ₆ N ₆	1	3	297	-	11	7	98.97	27.15
MP0096	n-type Si	C ₃ H ₆ N ₆	1	3	297	-	6	8	99.62	9.19
MP0086	p-type Si	C ₃ H ₆ N ₆	1	3	297	-	7.5	5	99.94	7.17

EXPERIMENTAL

SAMPLE PREPARATION

Diamond deposition was performed in an ASTeX microwave plasma chemical vapor deposition (MPCVD) system. Hydrogen and methane were used as precursor gases. The gas flow rates of hydrogen, methane, and nitrogen were varied depending on the sample. The melamine powder was heated and the vapor was delivered to the chamber. The microwave power was 1050 W and the total pressure of the chamber ranged between 28 - 30 Torr. The deposition temperature, monitored by an optical pyrometer, was measured to be approximately 800 °C. The summary of sample preparation conditions are described in Table 1.

CHARACTERIZATION

The sample was characterized by scanning electron microscopy (SEM), micro-Raman spectroscopy, photoluminescence spectroscopy (PL), optical microscopy, and field emission measurements. The Raman and photoluminescence analyses were performed with the 514.5 nm line of an Ar ion laser. The measurement was carried out at room temperature, and the Raman system was configured to allow a spectral resolution of 0.2 cm⁻¹.

RESULTS AND DISCUSSIONS

DEGRADATION OF DIAMOND QUALITY UPON NITROGEN ADDITION

It is considered difficult to incorporate large amounts of substitutional nitrogen impurities into growing CVD diamond without negatively affecting the growing film. Previous research has shown that adding nitrogen during diamond growth can deteriorate the quality of the diamond film by enhancing the formation of graphitic and other nondiamond phases [7]. It was reported that even a small amount of nitrogen gas in the reactor can produce non-diamond carbon phases, resulting in a broadened diamond Raman peak at 1333 cm⁻¹. As nitrogen is added into the growing diamond, the morphology of the sample changes from well-faceted crystals to fine grained crystals. The effect of large amounts of nitrogen incorporation into a CH_4/H_2 system has been investigated by Badzian *et al.* [8]. They found that the addition of 20% N₂ to the reactor with 1% CH_4 in H₂ can completely inhibit the diamond growth.





show the effect of nitrogen addition into the photoluminescence spectra of diamond on growing diamond film

FIG. 3 A series of Raman spectra which FIG. 4 The effect of nitrogen addition on silicon.

Figure 3 shows a series of Raman spectra which exhibit the effect of nitrogen addition into the growing diamond film. As nitrogen is added into the growing diamond, the intensity of the 1332 cm⁻¹ diamond peak is decreased. A large amount of graphitic carbon was observed when the concentration of the nitrogen was 0.5 - 1%. At high nitrogen concentrations (2%), only small amount of graphitic phases are detected. It is speculated that different mechanisms govern at low and high nitrogen concentration regimes. As shown in the figure, the 1333 cm⁻¹ diamond Raman peak broadens as nitrogen was added into growing diamond. A peak at around 1195 cm⁻¹ is known as a peak related to C-N bond vibration [10].

Figure 4 shows the effect of nitrogen addition on photoluminescence spectra of diamond on silicon. Raman spectrum from diamond, graphitic phases, and C-N vibration are shown at low wavenumber regions. PL spectra show that a negligible amount of nitrogen is incorporated into the diamond during the growth when nitrogen was used as a nitrogen source. The nitrogen related peaks at 2.154 eV (2065 cm⁻¹) and 1.945 eV (3750 cm⁻¹) can barely be seen in the spectrum of nitrogen-doped diamond. The detailed description of nitrogen related PL peaks are discussed in next section.

NITROGEN DOPING WITH MELAMINE

The Raman spectrum (Figure 5) revealed a sharp peak at 1333 cm⁻¹. The full width at half maximum (FWHM) of the nitrogen-doped sample, grown with melamine, is around 5 cm^{-1} , which is considered to be relatively small in CVD diamond. Similar results were observed from other samples doped with nitrogen using melamine as the precursor. A small signal of graphitic phase was observed at around 1500 cm⁻¹. This is negligible because the sensitivity of the Raman signal of graphite is about 200 times stronger than that of diamond when the 514.5 nm line of Argon ion laser is employed for excitation [10]. A broad peak at around 1195 cm⁻¹ was also observed in our spectra, which can be related to C-N bond vibration [10]. The diamond 'quality factor' (Q_{514.5}) for Raman spectra, using the 514.5 nm line of Argon ion laser excitation, was introduced by Sails *et al.* [11]. As shown in Table 1, higher Q-factors were obtained from nitrogen doping using a melamine source than using pure nitrogen.



FIG. 5 Raman spectra of the nitrogendoped diamond from melamine.

FIG. 6 Photoluminescence spectra of the nitrogen-doped diamond from melamine.

According to the PL spectrum shown in Figure 6, successful incorporation of the nitrogen into the diamond was achieved during growth. Nitrogen related optical centers with zero-phonon lines at 2.154 and 1.945 eV can be clearly seen in the figure. The 1.945 eV peak is related to a substitutional nitrogen-vacancy optical center [12], whereas the 2.154 eV peak could be due to an optical center composed of a single substitutional nitrogen atom with one or more vacancies [13]. The peak at 1.681 eV is considered to be due to the transition in a silicon complex center [14,15]. In order to semi-quantitatively analyze the concentration of substitutional nitrogen in the film, we introduce the nitrogen incorporation factor (NIF). The NIF is based on the substitutional nitrogen related peaks from photoluminescence spectra. NIF is expressed as follows;

$$\text{NIF} = \frac{A_{2.154} + A_{1.945}}{A_{\text{Diamond}}}$$

where $A_{2,154}$ and $A_{1,945}$ are the areas under the PL peak at 2.154 eV and 1.945 eV respectively, and $A_{diamond}$ is the area under the diamond Raman peak. For convenience, only two substitutional nitrogen related peaks were used in this factor. The NIF of these samples were compared to the NIF of the nitrogen-doped diamond film grown using pure nitrogen gas as the precursor. As seen in the Table 1, the NIF of the sample doped with melamine is higher than that of the sample doped with pure nitrogen, while the Raman FWHM of the former is smaller than that of the latter. Therefore, it is certain that nitrogen can be doped into the growing diamond from melamine without severe degradation of the crystal quality of the diamond.

FIELD EMISSION FROM NITROGEN-DOPED DIAMOND

Figure 7 shows the two types of field emission measurement system employed in this experiment. System (a) utilizes a grid anode with a polyester spacer separating the sample and anode. A movable anode rod was used in system (b). The edge of the rod was rounded to eliminate edge effects.



FIG. 7 Configurations of the FIG. 8 (a) I-V plot and (b) FN plot of nitrogen doped field emission measurement diamond systems.

Electron field emission data from two diamond films were compared. Sample-N (MP0122) was grown with H_2 , CH_4 , and N_2 . This film contains a small amount of substitutional nitrogen and large amounts of non-diamond carbon phases. Sample-M (MP0093) was synthesized with H_2 , CH_4 , and melamine ($C_3H_6N_6$). A large amount of substitutional nitrogen and a negligible amount of graphitic component were observed in this sample. Figure 8(a) shows the I-V characteristics from sample-N and sample-M. The field emission turn-on field of these films were approximately 90 V/µm. The samples were considered to be turned-on when the emission currents were higher than 10^{-10} amperes. The tunneling of electrons through the energy barrier under the intense electric field can be described by Fowler-Nordheim (FN) equation [16]. The Fowler-Nordheim equation expresses the current density as a function of applied electric field and work function of the metal. The FN equation can be expressed as follows [17,18];

$$J = AE^2 \phi^{-1} \exp[-B \phi^{3/2} / E]$$

where J is the current density, E is the applied electric field, ϕ is the work function of the metal, and A and B are constants. A FN plot (Figure 8(b)) shows no significant difference in the slops of the curves, which means that field emission work functions of these two samples are similar. Other samples did not show any significant difference in emission characteristics.

Contrary to other reports [2,3,5,6], nitrogen-doped diamond does not seem to exhibit a low onset field. Therefore, it is suggested that nitrogen incorporation into the diamond play a minor role in changing the electron emission properties. It is speculated that the back contact has a stronger influence on field emission properties than the nitrogen doping level.

CONCLUSIONS

Nitrogen-doped diamond films were prepared for the first time using melamine $(C_3H_6N_6)$ as a nitrogen source. As a comparison, nitrogen-doped diamond films were also produced using pure nitrogen gas. Relatively high amounts of substitutional nitrogen were successfully doped into diamond from melamine without degrading the quality of the diamond. However, when pure nitrogen gas was used as the nitrogen source, the quality of the diamond was degraded. Nitrogen-doping does not exhibit any dramatic enhancement in field emission characteristics of diamond. It is suggested that nitrogen incorporation into diamond only plays a minor role in enhancing the field emission properties of the material. It is speculated that the back contact has a stronger influence on field emission properties than the nitrogen doping level.

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