FIELD EMISSION CHARACTERISTICS OF DEFECTIVE DIAMOND FILMS

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ABSTRACT

The field emission characteristics of defective diamond films grown by microwave plasma enhanced chemical vapor deposition (MPECVD) have been studied. X-ray diffraction, The poor crystal quality and/or small grain sizes of the diamond phase and the inclusion of the non-diamond carbon phases in these films have been confirmed by raman spectroscopy, scanning electron microscopy, atomic force microscopy, and the reflectance measurements. The degrees of the film defectiveness and the emission characteristics were dependent on the methane concentration. Current-versus-voltage measurements have demonstrated that the defective diamond films have good electron emission characteristics. The observed correlation between the degrees of film defectiveness and the emission characteristics strongly suggests the defect-related electron-emission mechanism. The defective diamond films deposited on Si substrates show the field emission current density of 1μA/cm^2 and 1mA/cm^2 have been measured at electric fields as low as 4.5V/μm and 7.6 V/μm, respectively. We also observed the similar emission characteristics from the defective diamond film deposited on Cr/Si substrate and could decrease the deposition temperature to 600℃.

I. INTRODUCTION

Diamond is one of leading candidate for field emitter materials due to its low electron affinity, high thermal conductivity, high chemical inertness, and high physical strength, and there are numerous reports on this subject.[1-5] In spite of all these promising prospects, the diamond-based field emitters are still suffering from the problems such as high growth temperature, poor uniformity, and poor reproducibility. To overcome the current shortcomings without compromising their desirable properties, both the diamond-growth and the field-emission mechanisms have to be understood. However, the field emission mechanism from diamond-based emitters is far from being well understood, yet. Nevertheless, many current models emphasize the importance of the large field enhancement,[6] the conducting channels,[5] and the mid-gap states[7] of the diamond films. With the expectation that we can exploit one or more of the suggested mechanisms with defective diamond films, which have poor crystal quality and/or small grain sizes, and non-diamond carbon inclusions, we modified the conventional diamond deposition conditions accordingly. All of our defective diamond films have shown very good emission characteristics; high emission current densities at low voltages, good stability and reproducibility, and moderate emission uniformity.

II. EXPERIMENT

Diamond films were deposited on phosphorus doped *n*-type Si (100) wafers and Cr/Si wafers(Cr deposited about 3000Å on n-type Si) by the microwave plasma enhanced

CVD method using mixture gases of CH_4 and H_2. Methane concentrations in the gas mixtures were in the range of 1% to 4% except low temperature deposition. To increase the nucleation density, substrates were scratched with diamond powders prior to the deposition

X-ray diffraction (XRD) and Raman spectroscopy were used to evaluate the structural quality of diamond films. The XRD patterns were recorded using a Cu target with 0.02° resolution. The Raman spectra were excited using the 514.5 nm line of an Ar ion laser, and the spectra measured at a resolution of 2 cm^{-1} were accumulated over 5 scans. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to examine the surface morphology of the films. SEM was used also for the determination of the film thickness. Reflectance spectra of the films were measured using the calibrated reference mirror in the visible and near IR wavelength range.

The field emission characteristics were investigated by measuring I-V curves with an anode plate in a diode set-up and the actual emission images were also observed by using a phosphor-coated ITO glass as an anode. All the measurements were carried out in a vacuum chamber with a base pressure of 10^{-7} torr.

III. RESULT AND DISCUSSION

In Fig. 1, we have shown the results of the Raman spectroscopy and the x-ray diffraction of defective diamond films deposited Si wafer. The Raman spectra shown in Fig. 1 (a) are eminently different from those of the typical MPECVD grown diamond films; discernible diamond peaks were not resolved from these spectra. The main features of these Raman spectra are the broad peaks which are characteristic of DLC or amorphous carbon .with graphitic bonding. The weak feature near 1150 cm^{-1} has been suggested to stem from either the small crystallite size or disorder in a tetrahedral carbon network.[8, 9]

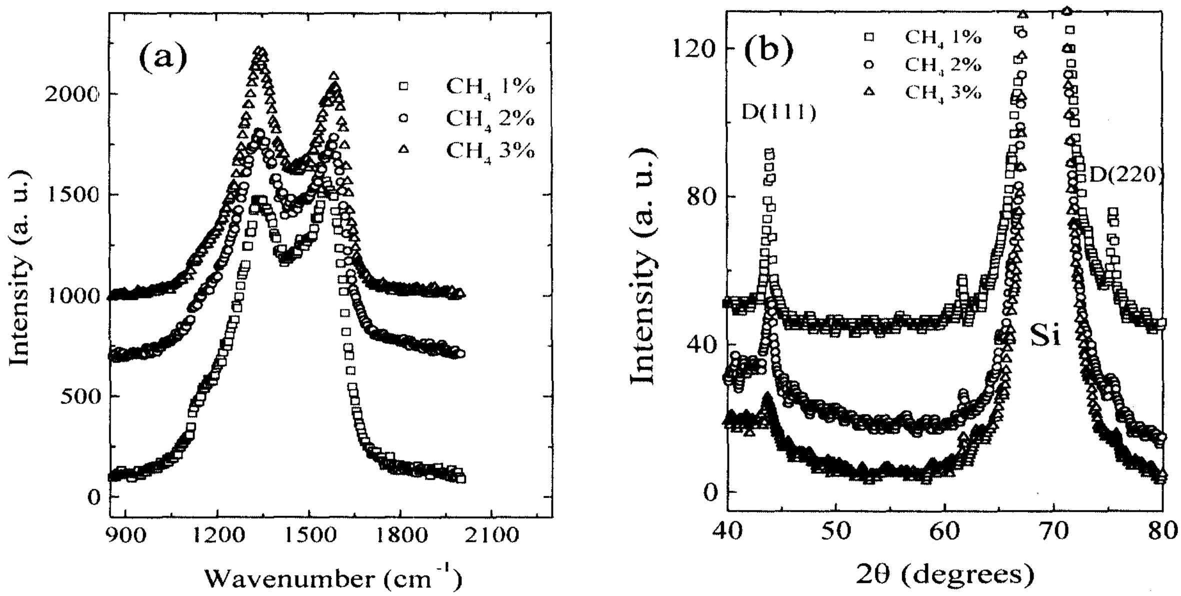

Fig. 1. A comparison of (a) the Raman and (b) the XRD spectra of defective-diamond films deposited at different CH_4 concentrations. Unmarked XRD peaks originate from Si substrates.

Unlike the Raman spectra, which did not exhibit discernible diamond peaks due to the large difference in the cross section between non-diamond component and diamond, the XRD result clearly showed diamond (111) and (220) peaks. However, as shown in Fig. 1 (b), diamond peaks have large FWHM, which becomes larger at higher methane concentration. All these observations indicate that our diamond films are defective with poor crystal quality and/or small grain sizes, and non-diamond carbon inclusions. We also find that the microscopic film structure (or degrees of film defectiveness) depends on the CH_4 concentration.

In Fig. 2 (a), we have shown a typical SEM micrograph and a AFM image of the diamond film deposited on Si wafer with 2% methane concentration. From SEM micrograph we find that our defective diamond film has a fine-textured surface with average grain size smaller than 60 nm. The defective diamond film deposited Cr/Si substrate has larger grain size. We have examined also the cross section of the film by SEM, and confirmed that the grain size is almost uniform throughout the film thickness. The film surface morphology is also investigated by AFM. The estimated root-mean-square (rms) roughness is about 7 nm, which seems to be underestimated due to the finite lateral resolution. Therefore, AFM confirms that our defective diamond film surface is very fine textured. SEM and AFM characterizations of other diamond films deposited at different methane concentrations exhibited similar results.

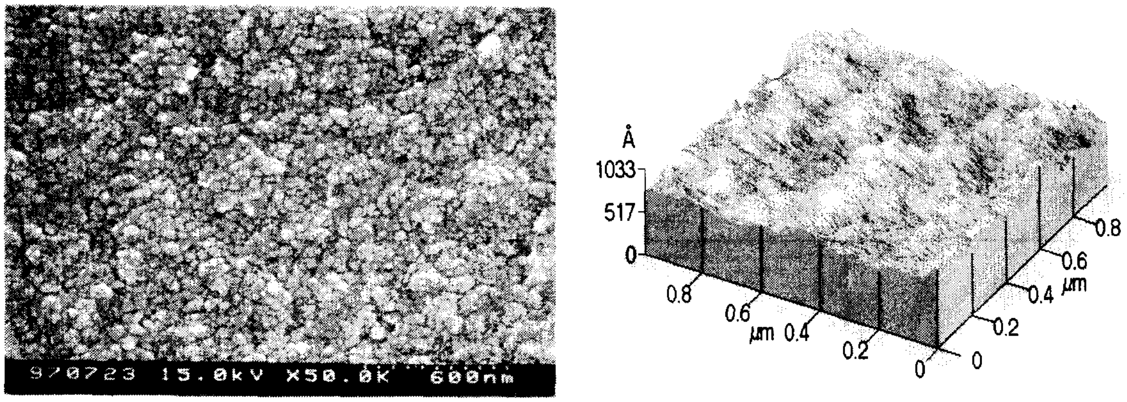

Fig. 2. A typical surface morphology of the diamond film deposited at CH_4 concentration of 2%: (a) SEM micrograph and (b) AFM image.

In Fig. 3, we have shown the emission I-V curves from the defective diamond films deposited on Si substrate with different methane concentrations at 800℃, which clearly illustrate the excellent field emission characteristics of these films; initiation of the field emission at very low field and large emission current density at relatively low applied field. In case of the film deposited at 2% methane concentration, which is the best emitting film, we measured the current densities of 1 $\mu A/cm^2$ and 1 mA/cm^2 at electric fields of 4.5 V/µm and 7.6 V/µm, respectively. It has to be emphasized that the emission current densities were estimated by averaging the measured currents over the entire sample areas. Therefore, the presented values of the current densities are lower limit values. A comparison of the I-V curves demonstrates the methane-concentration-dependent field emission behaviors of these films. In particular, it is very interesting to note that contrary to the increase of the methane concentration from 1% to 2 %, which improved the emission, the further increase of the methane concentration from 2% to 3% degraded the emission. Considering the results of the film characterization discussed above, the observed methane-concentration dependence of the emission must be associated with the degrees of the film defectiveness; the crystal quality and/or grain size and non-diamond inclusion must play an important role in the field-emission mechanism. The Fowler-Nordheim (F-N) plots corresponding to the measured I-V curves are shown in the inset. Usually, the linear F-N plot is indicative of the standard field emission. However, interestingly, the F-N plots exhibit two linear regions: the high and the low field regions, the origin of which is still unclear. In view of the emitting current saturation, we propose that the high field region must be related with the limited electron supply to the emitting sites.[13, 14]

Fig. 4 shows the test results for the reproducibility and the stability of the emission from the defective diamond films deposited on Si. As presented in Fig. 4 (a), the repeated emission produced similar current densities at each given emission field. Also, the emission field corresponding to the current density of 0.1 $\mu A/cm^2$ shows a small variation (see the inset). The temporal variation of the emission current is shown in Fig. 4 (b). In this figure, the current fluctuation is less than 5% at the average emission current of 26.9 μA. These test results suggest that the inclusion of the non-diamond component, which seems essential for the good emission characteristics, does not compromise the reliability of the defective-diamond-film-based field emitter.

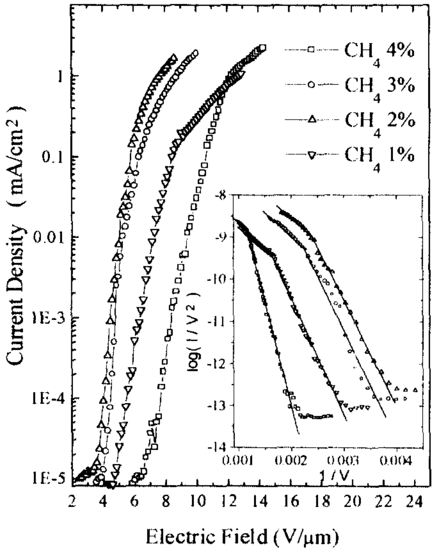

Fig. 3. Emission I-V curves of the defective diamond films deposited at various CH_4 concentrations. Corresponding F-N plots are shown in the inset.

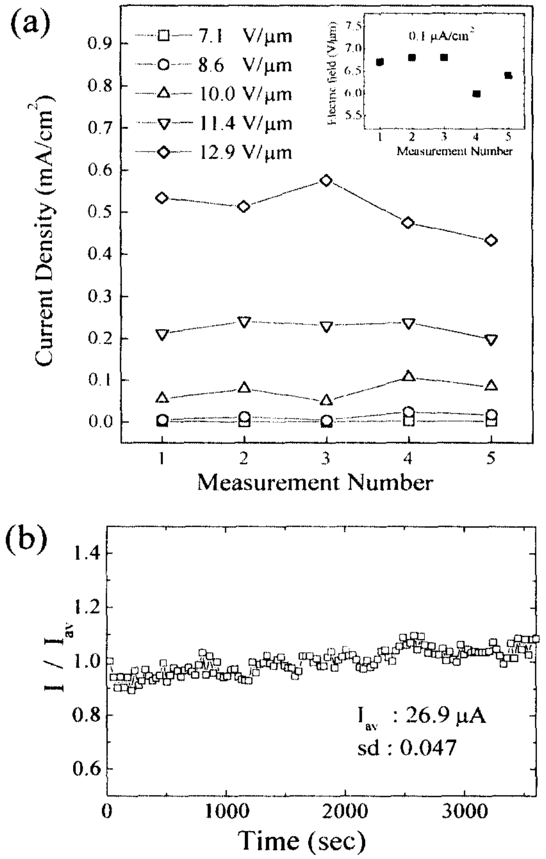

Fig. 4. Test results of the reproducibility and the stability of the emission from the defective diamond films. (a) Emission current densities were measured during the successive voltage ramping. The variation of the emission field to produce the current density of 0.1 $\mu A/cm^2$ is also shown in the inset. (b) The temporal variation of the emission current: fluctuation is less than 5% at the average emission current of 26.9 μA.

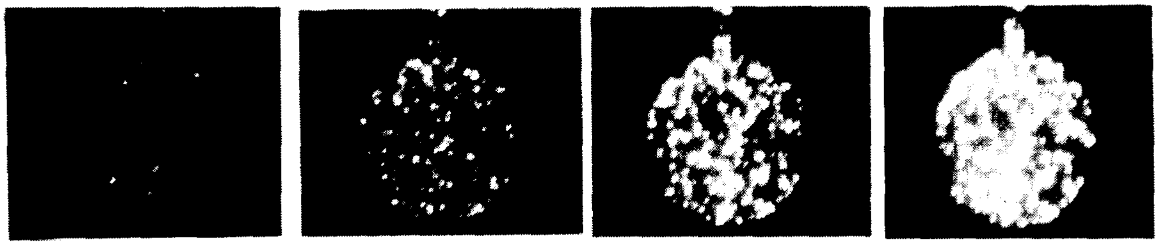
(a) 700 V (b) 800 V (c) 900 V (d) 1000 V

Fig. 5. The optical emission images of the defective diamond film deposited at CH_4 concentration of 2%. Four images at the bias voltages of (a) 700 V, (b) 800 V, (c) 900 V, and (d) 1000 V are shown. A phosphor-coated ITO glass is used as an anode to produce these 6-mm diameter images.

Fig. 5 shows one of the better emission images from the defective diamond films deposited at 2% methane concentration on Si wafer. To obtain these images, the film were covered with spacers with a 6-mm hole, and phosphor-coated ITO glasses were used as anodes. These images clearly show that the observed emission-current increase as a function of the voltage stems from the increase of the total number of emitting sites as much as the increase of the emission current per emission site. Both the non-uniform spatial distribution of the emitting sites and the field dependence of the total number of emitting sites are believed to be associated with the defective nature of our diamond films. In particular, the similar grain sizes (or surface roughness) of the diamond films deposited at different methane concentrations suggest that the distribution of non-diamond component plays a very important role in determining emission uniformity. The emission non-uniformity is one of the most important issues that have to be solved to utilize diamond-film-based field emitters for the flat panel display. However, the observed emission non-uniformity indicates that the actual emission current densities at emitting sites are much larger than what we have shown in Fig. 3.

Fig. 6 shows the emission I-V curve and F-N plot from the defective diamond film deposited on Cr/Si substrate with $50\mu m$ spacers. The deposition conditions are much the same and the field emission characteristics are similar to the diamond films deposited on Si wafers. It also has low turn-on voltage, high current density, and medium emission site density.

Fig. 7, shows the I-V curve from the defective diamond film deposited on Si wafer at 600℃. In contrast to the diamond film deposited at 800℃, this film shows higher turn-on voltage and lower emission current density. The lower deposition temperature films show

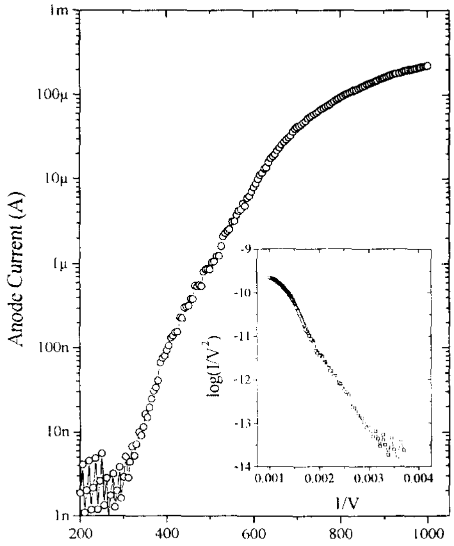

Fig. 6. Emission I-V curves of the defective diamond films deposited on Cr/Si substrate. Corresponding F-N plots are shown in the inset.

low emission characteristics specially with low emission density. However, it was still possible acquire the films which show the turn-on electric field lower than 20V/㎛.

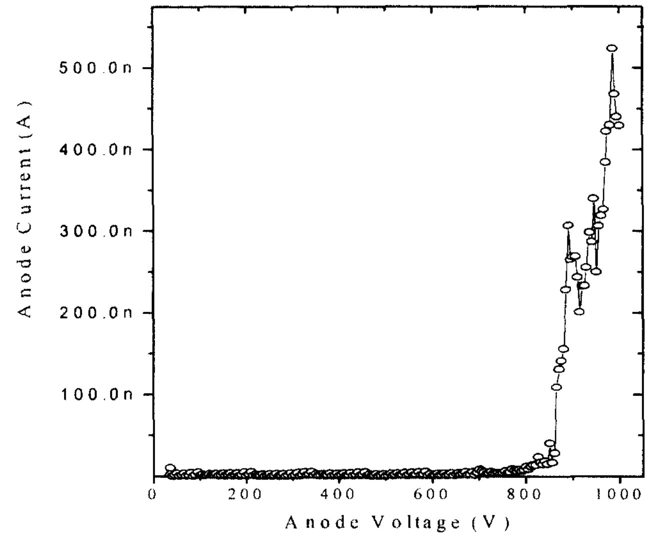

Fig. 7. Emission I-V curves of the defective diamond films deposited at 600℃.

IV. CONCLUSIONS

We have demonstrated that defective diamond films are promising as field emitters. Emission has been initiated at low voltages, and high emission current densities have been obtained. Also, emission from these films has been found reasonably reproducible and stable. The field emission characteristics from defective diamond films has exhibited dependence on the methane concentrations in the precursor gas mixture. Since the characterization of these defective diamond films by using various techniques has revealed the methane-concentration-dependent variations in the crystal quality and/or grain size and the content of the non-diamond inclusion, we conclude that the field-emission mechanism from diamond films is closely associated with the defects inside the film. Even though it is conceivable that the small grain size of our films has contributed to the good emission characteristics through large field enhancement, we conclude that the role of non-diamond inclusion is more important in field emission from defective diamond films. Our conclusion is based on the observation that the methane-concentration-dependent variation of the surface roughness is small as determined by SEM, AFM, and the reflectance measurement. However, Raman spectroscopy and the reflectance measurement have shown that there is a large variation in the content of the non-diamond inclusion as the methane concentration is increased. It is very interesting to note that there is a narrow methane-concentration window for the best emitting film deposition. The non-uniformity observed in the optical emission images also implies the importance of the non-diamond inclusion. Our all conclusion based on the observation of defective diamond films deposited on Si at high temperature.

We also conclude that metal films could be utilized as cathode substrates for defective diamond films and the deposition temperature could be 600℃ or below.

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