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FIELD EMISSION CHARACTERISTICS OF DIAMOND FILMS

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ABSTRACT

The field emission characteristics of diamond films deposited by microwave plasma enhanced chemical vapor deposition (MPECVD) method were investigated. Diamond films were deposited on n-type Si(100) wafer using various mixtures of hydrogen and methane gas, and the I-V characteristics are measured. We observed that the field emission characteristics depend on the CH_4 concentration and the diamond film thickness. All the films show remarkable emission characteristics;low turn-on voltage, high emission current density at lower voltage, uniform stable current density, and good stability and reproducibility. The threshold field for producing a current density of $1mA/cm^2$ is found as low as $7.6V/\mu m$.

INTRODUCTION

Field emission displays (FED) have been vigorously investigated for its great potential as flat panel displays in multi-media portable electronics. The partial list of the virtue of FED includes the low power consumption, the high brightness, the full color capacity, the wide viewing angle, and the high resolution, in addition to the advantage of being thin and light-weight. Typically FED are fabricated in either triode or diode type. Silicon or metal microtips are the most common examples of the triode type FED which exploit the advantage of high field enhancement factor. Even though they have very g ood emission characteristics, the difficulty of fabrication and the lack of stability and reliability hinders the wide application of the triode type FED. The diode type FED are much easier to fabricate, but usually the emission characteristics are not as good as their triode counterpart due to their very small field enhancement factor. Hence it is necessary to use the material with very low work function, for example diamond, as a field emitter in the diode type FED.

Recently, diamond has emerged as a desirable material for field emitters due to their low electron affinity(even negative), high thermal conductivity, high chemical inertness and high physical strength. There are

numerous reports of field emission from various diamond-based emitters. For example, W. Zhu[1] have studied field emission from undoped or p-type doped diamond, Ken Okano[2] have observed the lowest turn-on field from n-type doped diamond deposited by hot filament CVD, and N. Kumer[3] have studied armophic diamond cathode FED. In spite of the very wide research activities concerning the diamond field emission behaviors, the field emission mechanism from diamond is not fully understood, yet. However P. H. Cutterler[4] showed that electrons are transported though the energy state which is just below the minimum of conduction band gap from the theoretical calculation, and N. S. Xu [5] also sho-wed that dielectric breakdown and graphite inclusions could form the conducting channel. On the other hand, W. Zhu[6] have found that the improved emission characteristics of the ion-implanted diamond is due to the defects created by the ion implantation process.

In spite of their very promising emission characteristics, high current density at low electric field, diamond suffers from the following shortcomings; high growth temperature, poor current density uniformity, and poor reproducibility of turn-on field. One popular strategy to overcome the above shortcomings of the diamond emitter has been to find a good substitute for diamond. Therefore, a great deal of attention has been paid to the emission studies of diamond like carbon (DLC) films. But it turns out that DLC films have their own shortcomings; higher turn-on field, lower emission current density, and susceptible to damage.

In this study, we deposited diamond films at various CH_4 concentrations by MPECVD method and measured I-V characteristics. We controlled our deposition conditions in such a way that we can exploit any of the suggested emission mechanisms. All of our films showed remarkable emission characteristics; low turn-on voltage, high emission current density at lower voltage, uniform current density, and good stability and reproducibility.

EXPERIMENTAL

Diamond films were deposited on phosphorus doped Si (100) wafers using the microwave plasma enhanced CVD method. To increase the nucleation density, Si wafers were scratched by diamond powders prior to the deposition. CH_4, H_2, and O_2 were used as source gases. A series of diamond films were deposited at various CH_4/H_2 concentrations for the fixed deposition time. We also varied the deposition time at the fixed CH_4/H_2 concentration to observe the thickness-dependent effects. Finally, a film is prepared from the O_2-added source gas. The sample preparation conditions are presented in Table 1 together with the summary of the field emission characteristics of all the diamond films.

Scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy were employed for the structural characterization of the diamond films. Especially, we examined the surface morphology, crystallinity, defect content, and the nature of the carbon bonding in MPECVD deposited films.

The field emission characteristics were investigated by measuring I-V curves with a diode set-up. The measurements were carried out in 10^{-7} torr vacuum, while the external DC voltage was supplied by the Keithley 237

Table 1. Deposition conditions and field emission characteristics of diamond films

Sample ID	CH_4/H_2	O_2/CH_4	Deposi tion time(hour)	Electric field (V/μm)		Comment
				Turn-on (1μA/cm²)	Thres hold (1mA/cm²)	
#1	0.5%		3			no emission
#2	1%		3	6.3	12.7	
#3	2%		3	4.5	7.6	
#4	3%		3	4.8	8.8	
#5	4%		3	8.3	12.2	
#6	2%		4	7.3	14.2	
#7	2%		5	7.5	15.3 *(593μm/cm²)	voltage source limit
#8	2%	50%	3	8.9	15.3 *(196μm/cm²)	voltage source limit

high voltage source and measurement unit. The distance from the stainless steel anode to the diamond film was kept at 70μm by the spacer.

RESULT AND DISCUSSION

All the SEM pictures show that our MPECVD diamond films have a continuous and relatively smooth surfaces. It is worth while to emphasize that even after the prolonged emission tests, there are absolutely no sign of the diamond surface damage based on the comparison of the SEM pictures taken before and after the emission test, respectively. This clearly distinguishes our films from the DLC films. We show the typical XRD patterns of our diamond films in Fig. 1. In this figure, we find only the (111) and the (220) peaks of the diamond, which confirms that our field-emitting films are really diamond films. However, it is quite interesting to note that the films with good emission characteristics exhibit only the (111) peak but the films with poor emission characteristics exhibit both the (111) and the (220) peaks, and that even the (111) peak quality is better in the poorly emitting films; narrower FWHM and larger intensity. This observation strongly suggest that either the defect or the included impurity phase play an important role in the field

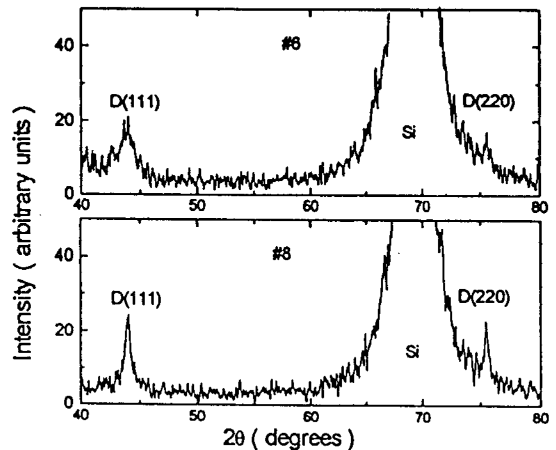

Fig. 1 XRD patterns of MPECVD deposited diamond films.

emission as discussed above. Raman spectroscopy results also confirm the existence of the diamond phase. But we also find the Raman features that correspond to the SP2 and SP3 carbon bondings with various degrees of imperfection. Once again, the Raman spectra suggest that not necessarily the best quality diamond film is the best field emitter.

In Fig. 2, we show the variation of the I-V characteristics of the films deposited at different CH_4 concentrations. Except the non-emitting film #1 which is deposited at 0.5% CH_4 concentration, all other films start to emit at very low field and show relatively large emission current density at moderate applied field. The values of the turn-on and the threshold field which is defined as the field that corresponds to the current densityof 1 $\mu A/cm^2$ and 1 mA/cm^2, respectively, are summarized in Table 1. The range of our turn-on field, between 4.5 V/㎛ and 8.3 V/㎛, and of the threshold field, between 7.6 V/㎛ and 12.7 V/㎛, are low enough to make our diamond film a good candidate for the flat emitter in a diode type FED.[7] Based on the observed variation of the turn-on and the threshold field, we conclude that the diamond film deposited at 2% CH_4 concentra tion has the best emission characteristics. We also conclude that CH_4 concentration is one of the determining factor for the emission characteristics due to the change in the diamond film quality as we find in our structural investigation.[8, 9]

Field emission is well described by the Fowler-Nodheim (F-N) equation which can be expressed as follows;

$$\log\left(\frac{I}{V^2}\right) = \log a - b\frac{1}{V} \quad (1)$$

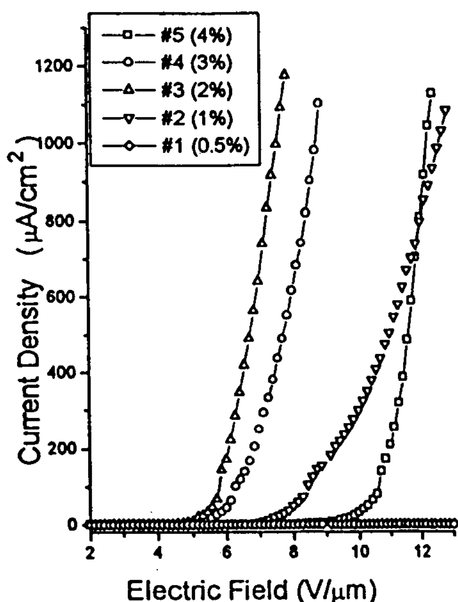

Fig. 2 The I-V curves of the films deposited at different CH_4 concentratins

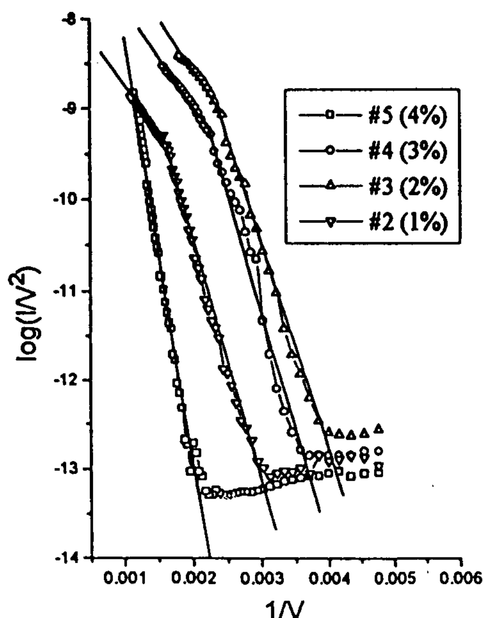

Fig. 3 The F-N plots of the measured I-V curves of the films deposited at different CH_4 concentratins.

where V is the applied voltage and I is the emission current. Hence, if we plot $\log\left(\frac{I}{V^2}\right)$ versus $\frac{1}{V}$, we can determine the constants a and b from the slope and the intercept of the straight line. However, the F−N constants a and b depend on the effective emitting area, the field enhancement factor, and the work function of emitting surface;

$$a = 1.4 \times 10^{-6} \frac{\alpha \cdot \beta^2}{\Phi} \cdot \exp\left(\frac{9.87}{\sqrt{\Phi}}\right) \quad (2)$$

$$b = 2.84 \times 10^{7} \frac{\Phi^{3/2}}{\beta} \quad (3)$$

where α (cm^2) is the effective emitting area, β (cm^{-1}) is the field enhancement factor, and Φ (eV) is the work function. In Fig. 3, we present the F-N plots of the measuredI-V curves. The linear relationship between log $\left(\frac{I}{V^2}\right)$ and $\frac{I}{V}$, strongly suggest that the mea sured currents are due to the tunnelling. But interestingly for the films #2, #3, and #4, the F-N plots show two linear regions; the high and the low field regions. The similar F-N plots with dual linear slopes from diamond -based emitters have been reported previously[10], but the origin of the observed phenomena is still unclear. In Table 2, we summarize the values of the F-N constants a and b in the high and the low field regions, respectively. An attempt to determine the effective emitting area, the field enhancement factor, and the work function of emitting surface is under progress.

In Fig. 4, we show the results of the repeated emission measurement from the single sample. We measured the emission five times as follows; (increase V up to 900 V and measure I-V; e1)→turn off the voltage→(increase V up to 1000 V and measureI−V;e2) →turn off the voltage→(increase V up to 1100 V and measure I−V; e3→(maintain emission at 700 V for 10 min.)→ turn off the voltage→(increase V upto 900 V and measure I-V; afe1)→turn off the voltage→(increase V up to 900 V and measure I−V; afe2)→turn off the voltage. Figure 4 clearly demonstrates that our diamond films have the very stable and reproducible emission characteristics; the turn-on field and the current density. However, it was found

Table 2. The F-N constants a and b in the high and the low field regions.

Sample	Low electric field		High electric field	
ID (CH_4)	a	b	a	b
#2 (1%)	6.2×10^{-6}	2635	2.0×10^{-8}	1054
#3 (2%)	5.73×10^{-4}	2421	3.44×10^{-7}	1044
#4 (3%)	1.11×10^{-3}	2454	1.65×10^{-7}	1085
#5 (4%)	2.95×10^{-4}	4640		

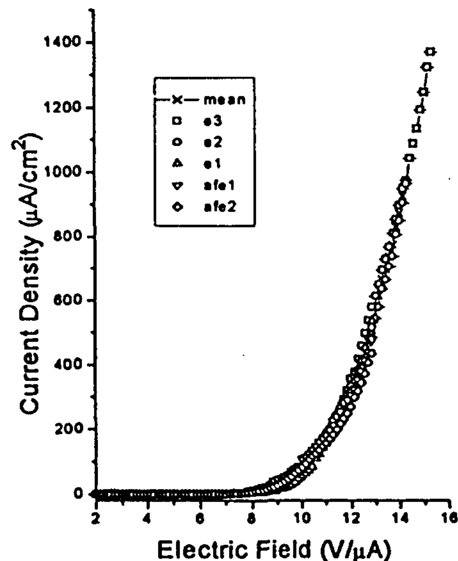

Fig. 4 The stability and repoducibility of the emession characteristics; the resuts of the repeated emission measurement from the single sample.

that both the reproducibility and the stability of the emission from the thicker films are not as good as those in thiner films. For example, the film #7 showed degraded emission characteristics in the repeated measurement after the previous 10 min. emission at 1000 V. The cause for the degradation in conjunction with the structural change is under study.

Finally, in Fig. 5 we compare the I-V curves of the films which were deposited from the identical source gases but have different thicknesses. Here we find that thethicker films have the inferior emission characteristics to their thinner counterparts. Whether the difference in the barrier thickness is solely responsible for the observed phenomena is unclear and it warrants the continued study.

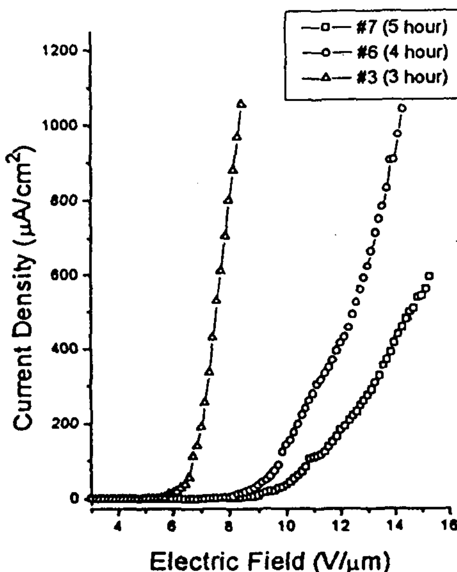

Fig. 5 The film thickness-dependent emission characteristics.

CONCLUSIONS

We deposited diamond films on the n-type Si by MPECVD method. Our diamond films exhibit remarkably low turn-on voltage, high emission current density, and good uniformity. Also, our diamond films have very stable and reproducible emission characteristics. We find that the CH_4 concentration and film thickness are the most important factors that determines the emission characteristics. Based on our observation, we conclude that not necessarily the best quality diamond film is the best field emitter; the defect or the included impurity phase play an important role in the field emission. The continued study to determine the effective emitting area, the field enhancement factor, and the work function of emitting surface from the F-N constants *a* and *b*, and to establish the relationship between the structure and the emission characteristics are under progress.

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