Effect of Diamond-Like Carbon Coating on the Emission Characteristics of Molybdenum Field Emitter Arrays

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***Abstract*—We have studied the electron emission characteristics of Mo field emitter arrays (FEA's) using a diamond-like carbon (DLC) film deposited by a layer-by-layer technique using plasma enhanced chemical vapor deposition. The turn-on voltage was lowered from 55 to 30 V by a 20-nm thick hydrogen-free DLC coating and maximum emission current was increased from 166 to 831 μA. Also the gate voltage required to get the anode current of 0.1 (μA/emitter) decreases from 77 to 48 V. Furthermore, the emission current from DLC coated Mo FEA's is more stable than that of noncoated Mo FEA's.**

***Index Terms*—Emission current, emission stability, hydrogen-free DLC, Mo FEA's PECVD.**

I. Introduction

FIELD emitter arrays (FEA's) have been emerging as micron-size electron sources for a number of advanced and new generation devices such as field emitter displays (FED's), ultrahigh-frequency devices, and so on [1], [2]. FEA's can be made more reliable and efficient by sharpening the emitter tips, reducing the emitter to gate distance and holding this dimension to a high tolerance, using lower work function emitter materials, and improving uniformity and reproducibility [3], [4].

Diamond films possessing negative electron affinity (NEA) [5] have great potential in their application as electron emitters in vacuum microelectronics such as FEA's and have attracted extensive studies. The interest in diamond-like carbon (DLC) as an emission material originates from its unique emission properties at low work function as well as stable operation. In addition, a high current can be obtained because of its high thermal conductivity.

Cold cathode electron emitters obtained by depositing diamond films on Si FEA's [6], Mo FEA's [7], or W FEA's [8] have been widely studied. The field strength required for electron field emission has been reduced to less than 3×10^4 V/cm, which is substantially lower than the field strength used in the conventional metal FEA's, typically higher than 1×10^6 V/cm [9].

DLC films can be deposited by various growth methods such as plasma-enhanced chemical vapor deposition (PECVD) and filtered vacuum arc deposition (FAD). Chuang *et al.* [9] have already reported about DLC coated by laser ablation process onto Mo FEA's. The DLC layer has the problem of emission instability because the surface properties of the DLC films are deteriorated by the local heat during operation.

In this work, we have fabricated hydrogen-free DLC films by a layer-by-layer technique using PECVD [10], and studied the emission characteristics of Mo FEA's with the DLC films. Finally, we discuss the influence of the quality of the DLC films on Mo FEA's.

TABLE I
LAYER-BY-LAYER DEPOSITION CONDITION FOR THE DLC FILMS

Condition	Deposition	CF_4 plasma exposure
rf power (W)	100	100
Pressure (mTorr)	20	25
Flow rates (sccm)		
He	50	50
H_2	5	0
CH_4	1	0
CF_4	0	30
Substrate temperature (K)	300	300
Time (seconds)	100	200

II. Experimental

Mo FEA's were fabricated by electron-beam evaporation of a molybdenum source onto an Si substrate. The arrays of 1.5-μm-diameter holes spaced on 10-μm centers were produced by the sequential processes of wet oxidation, Mo deposition, and Al coating, followed by patterning the gate layers [1]. During DLC deposition using conventional PECVD system, the substrate temperature was maintained at room temperature under a pressure of 20 mTorr. CH_4/H_2/He and CF_4/He gases were introduced for the deposition of the DLC layer and surface treatment, respectively. Table I depicts the layer-by-

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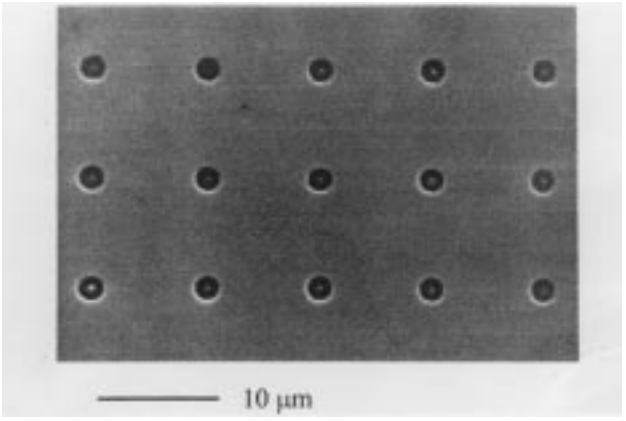
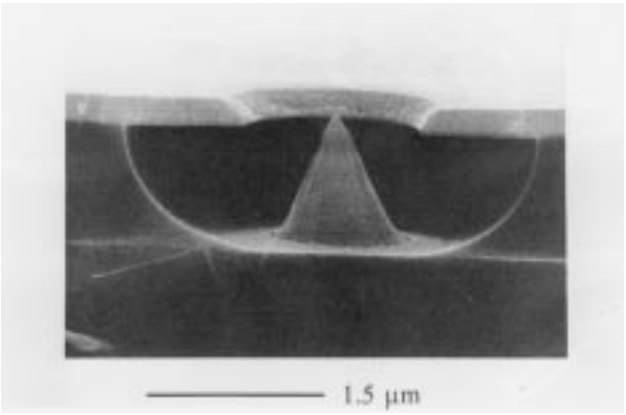


(a)



(b)

Fig. 1. The top view (a) of DLC coated Mo FEA's and the cross-sectional view (b) of a DLC coated Mo field emitter.

layer deposition conditions for the DLC films. We obtained 5-nm thick DLC layer for the 100 s and then performed surface treatment under CF_4 plasma for 200 s so that CF_4 plasma can remove effectively the weak bonds, such as predominantly C-H_n bonds and graphite C-C bond [11]. We repeated five cycles of the deposition and plasma exposure to obtain 20-nm thick DLC films.

In order to characterize the quality of our DLC films, we prepared 200-nm-thick DLC films that would present strong absorption peaks in a Fourier transform infrared (FTIR) analysis. The stretching mode absorptions due to CH_n $(n = 1, 2, 3)$ were investigated and hydrogen content was calculated using the absorption coefficient [12]. In addition, interband optical absorption coefficients were measured using a Perkin-Elmer UV-VIS-IR spectrophotometer and then from the data obtained the optical band gap was determined using Tauc's plot [13].

Electron emission characteristics of the FEA's were measured using a triode geometry. An anode plate was placed at a distance of 1 mm above the gate and was biased to $+300$ V. Both the anode and the gate currents were measured as a function of gate-to-cathode bias voltage using a Kiethley SMU 237 under a vacuum of 1×10^{-8} Torr. During the measurement, the device was in a common emitter configuration with the emitter grounded and both the anode and gate being positive potentials.

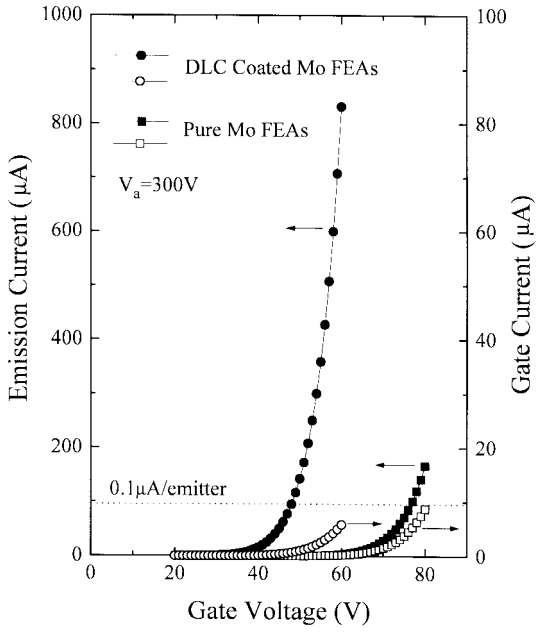


Fig. 2. Comparison of the *I–V* characteristics between DLC coated Mo FEA's and conventional Mo FEA's.

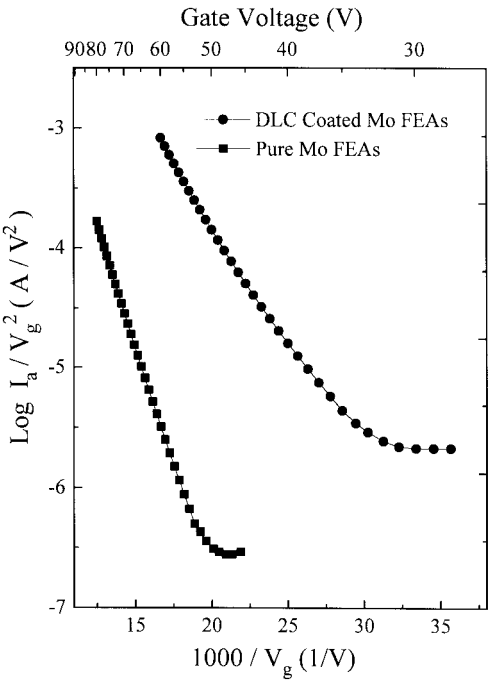


Fig. 3. F–N plots of both the DLC coated Mo FEA's and conventional Mo FEA's.

III. Results and Discussion

The morphologies of the DLC coated Mo FEA's observed by scanning electron microscopy are shown in Fig. 1. The cross-sectional view of the DLC coated Mo FEA's, as shown in Fig. 1(b), reveals that the emitter is typically 1.6 μm high and the gate aperture is 1.5 μm wide. The thicknesses of thermal SiO_2 and DLC layer were 1.2 μm and 20 nm, respectively.

Fig. 2 shows the emission current-voltage characteristics for the DLC coated Mo FEA's and noncoated Mo FEA's

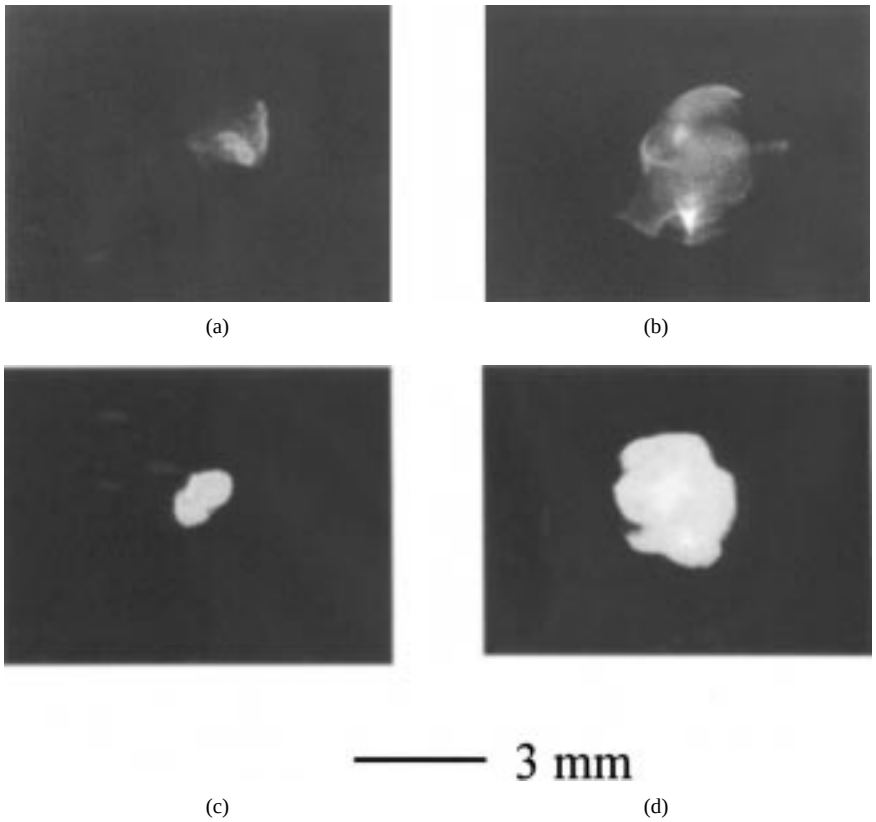


Fig. 4. Photographs of light emissions of Mo FEA's [(a) $V_g = 55$ V and (b) $V_g = 77$ V] and DLC coated Mo FEA's [(c) $V_g = 30$ V and (d) $V_g = 48$ V].

composed of 900 emitters. The turn-on voltage decreases from 55 to 30 V by DLC coating. In addition to the decrease in turn-on voltage, the maximum anode current is also increased from 166 to 831 μA. And the anode current of 0.1 μA per emitter can be achieved at 48 V in DLC coated Mo FEA's, while the same current level is obtained at 77 V in Mo FEA's. This fact indicates that the operating voltage can be remarkably decreased by adopting DLC layer on Mo FEA's. The gate current is less than 0.7% of the anode current for the DLC coated Mo FEA's, but 5.25% for Mo FEA's at the maximum gate voltage. The gate current increases monotonously with the applied gate voltage, but it starts at lower gate voltage in DLC coated Mo FEA's as compared to conventional Mo FEA's.

Fig. 3 shows Fowler–Nordheim (F–N) plots for the DLC coated Mo FEA's and Mo FEA's without DLC film. The field enhancement factor (β) for the emitter was first obtained by comparing ϕ value calculated from the slope of the F–N plots [1] of the Mo FEA's with the work-function reported for Mo metal (4.5 eV). With the form of the relation between log (I/V^2) and $1/V$, F–N equation is simply expressed as

$$\log(I/V^2) = A - B\phi^{3/2}/V \tag{1}$$

where ϕ(eV) is the work function of emitter materials. The slope of F–N plots S is inversely proportional to the geometrical factor $\beta(\mathrm{cm}^{-1})$ and expressed in

$$S = 2.82 \times 10^7(\phi^{3/2}/\beta). \tag{2}$$

The relation between the work function $\phi_{\mathrm{Mo}}, \phi_{\mathrm{DLC}}$ and the slope of F–N plots $S_{\mathrm{Mo}}, S_{\mathrm{DLC}}$ can be derived from (2) for two kinds of FEA's and expressed in

$$(\phi_{\mathrm{Mo}})^{3/2}/(\phi_{\mathrm{DLC}})^{3/2} = S_{\mathrm{Mo}}/S_{\mathrm{DLC}}. \tag{3}$$

The effective ϕ value calculated for the DLC coated FEA's is 2.10 eV, which is much less than typical value of Mo. Hence, we conclude that the work function of Mo FEA's seems to be lowered by the thin DLC coating.

Fig. 4 shows the photographs of the light emitting patterns of both Mo FEA's and DLC coated Mo FEA's with pixel area of 300 $\times$ 300 μm^2 with ZnO : Zn phosphor placed on anode plate in an UHV chamber. For Mo FEA's without DLC film, the threshold gate voltage of the light emission is about 55 V and the sufficient luminescence is observed beyond 77 V as shown in Fig. 4(a) and (b). In case of DLC coated Mo FEA's, as shown in Fig. 4(c) and (d), the former is obtained at the gate voltages of 30 V and the latter is observed beyond 45 V. Furthermore, the light emission patterns from DLC coated FEA's are found to be more stable and uniform compared to conventional Mo FEA's as shown in Fig. 4(b) and (d).

Fig. 5 shows the emission current fluctuations with the operating time for both DLC coated Mo FEA's and Mo FEA's without DLC film under the fixed stress field giving almost the same current level. There is a current variation of 0.9% for the DLC coated Mo FEA's and 8.9% current variation for the conventional pure Mo FEA's. A distinctive feature is that variations in the average current are very small for the DLC coated arrays, although there is a slight fluctuation in instantaneous current. Here, it is noticeable that the emission current of a few 100 μA maintained over a period of several hours for the DLC coated Mo FEA's.

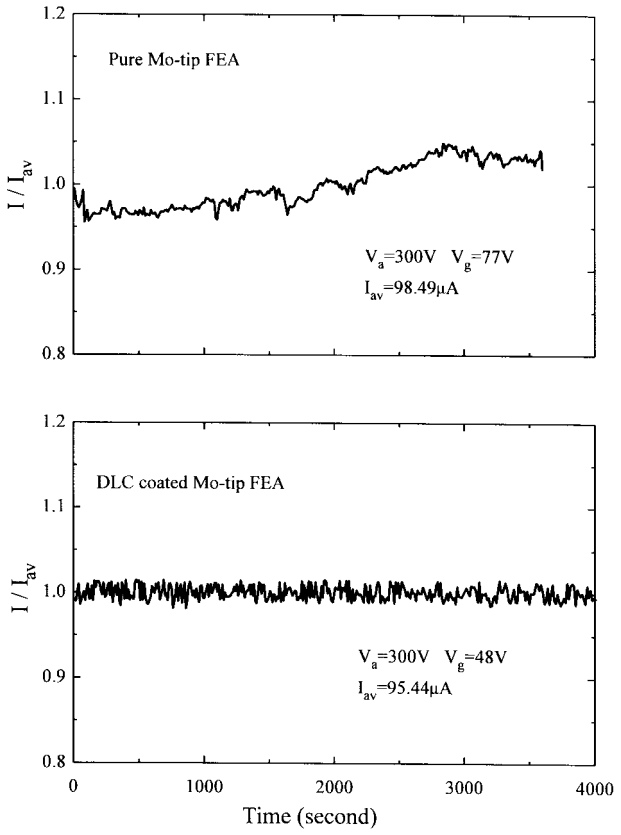


Fig. 5. The emission current fluctuations of both Mo FEA's and DLC coated Mo FEA's.

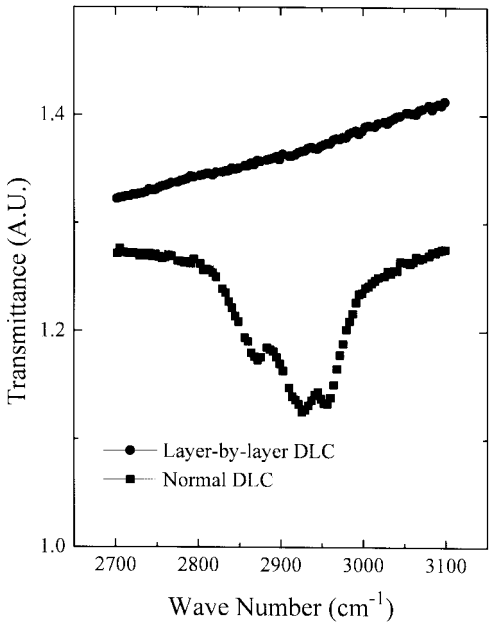


Fig. 6. Typical FTIR spectra for the deposited DLC films.

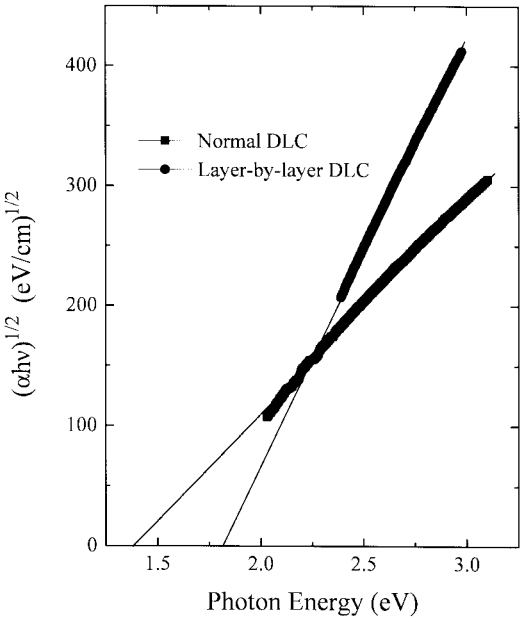


Fig. 7. Optical band gap of the deposited DLC films.

In order to characterize our DLC films that are effectively functioned for the enhancement of emission characteristics, we measured optical and electrical properties. Fig. 6 shows the FTIR transmittance spectra of the DLC films. The absorption peaks at 2870, 2925, and 2960 cm^{-1} corresponding, respectively, to sp^3 CH_3 (symmetrical), sp^3 CH_2 (asymmetrical) and sp^3 CH_3 (asymmetrical) modes [14]. As can be seen from the figure, the CH_n vibration peak disappears completely after the 200 s CF_4 plasma exposure. The hydrogen content estimated from the absorption coefficient [12] for the DLC films without CF_4 plasma exposure is about 25 at.%. However, the hydrogen content for the CF_4 plasma exposure DLC films is less than 1 at.%. Therefore, we confirm that a hydrogen-free DLC film on the Mo FEA's can be obtained using the layer-by-layer deposition technique.

Fig. 7 shows the optical band gap $(E_g^{\rm opt})$ of DLC film obtained from Tauc's plot. The optical band gap increases from 1.4 to 1.8 eV with CF_4 plasma exposure. Therefore, it is probable that the preferential etching contributes to increase in the optical band gap of the DLC film [11]. Considering the fact that the bonding and antibonding states of C-C sp^2 lie in the inner side of those for C-C sp^3 [15], the removal of the sp^2 bonds results in the widening band gap of the DLC. The etching process is as followed: the CF_4 plasma break bonds at the outmost of the layer of DLC and thus relax the remaining coordination. During the process the weak C-C bonds and H-C atoms can be easily broken by F radicals.

Fig. 8 shows the temperature dependence of dark conductivity of the DLC films. The slope of log conductivity versus $1000/T$ shows the activation energy increase from 0.25 to 0.55 eV with the CF_4 plasma exposure. This fact means that the Fermi level moves toward the midgap after CF_4 plasma exposure so that the barrier for electron emission is effectively lowered. As a result, the Fermi level appears to move toward the midgap due to the remarkable change of the material composition [10].

IV. Conclusion

We have studied the effect of a hydrogen-free DLC coating on the emission characteristics of Mo FEA's. The DLC

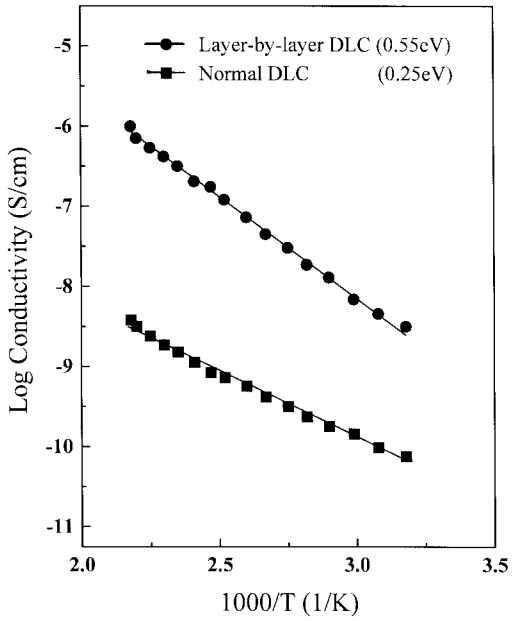


Fig. 8. Temperature dependence of conductivity for the deposited DLC films.

layer in the present work was prepared by a layer-by-layer deposition technique. The electron emission characteristics are improved by the thin DLC layer deposited onto Mo FEA's, moreover the stability is improved by adopting hydrogen-free DLC. It is important to use hydrogen-free DLC instead of conventional DLC, because the conductivity activation energy and the optical band gap increase with CF_4 plasma exposure. Therefore, the PECVD used in the present work can be applied to deposit large area and uniform DLC films with low cost, and our DLC can be applied to the mass production of FED's.

REFERENCES

[1] C. A. Spindt, I. Bodie, L. Humphrey, and E. R. Westerberg, "Physical properties of thin-film field-emission cathode with molybdenum cones," *J. Appl. Phys.*, vol. 47, p. 5248, 1976.

[2] P. Vaudaine and R. Meyer, "Microtips fluorescent display," in *IEDM Tech. Dig.*, 1991, p. 197.

[3] H. H. Busuta, J. E. Pogemiller, and B. J. Zimmerman, "Scaling of emission currents and of current fluctuations of gated silicon emitter esembles," *J. Vac. Sci. Technol. B, Microelecton. Process. Phenom.*, vol. 12, no. 2, p. 689, 1994.

[4] M. Nakamoto, T. Hasegawa, T. Ono, T. Sakai, and N. Sakuma, "Low operation voltage field emitter arrays using low work function materials fabricated by transfer mold technique," in *IEDM Tech. Dig. '96*

[5] , 1996, p. 297.

[6] F. J. Himpsel, J. A. Knapp, and J. A. Van Vechten, "Quantum photoyield of diamond(111)—A stable negative-affinity emitter," *Phys. Rev. B, Condens. Matter*, vol. 20, no. 2, p. 624, 1979.

[7] J. Liu, V. V. Zhirnov, A. F. Myer, G. J. Wojak, W. B. Choi, J. J. Hren, S. D. Wolter, T. McClure, B. R. Stoner, and J. T. Glass, "Field emission characteristics of diamond coated silicon field emitter," *J. Vac. Sci. Technol. B, Microelecton. Process. Phenom.*, vol. 13, no. 2, p. 422, 1995.

[8] W. B. Choi, J. Liu, M. T. McClure, A. F. Myers, J. J. Cuomo, and J. J. Hren, "Field emission characteristics of diamond coated molybdenum field emitter," in *Proc. 8th Int. Vacuum Microelectronics Conf.*, 1995, p. 315.

[9] N. Liu, Z. Ma, X. Chu, T. Hu, Z. Xue, X. Jiang, and S. Pang, "Fabrication of diamond tips by the microwave plasma chemical vapor deposition technique," *J. Vac. Sci. Technol. B, Microelecton. Process. Phenom.*, vol. 12, no. 3, p. 1712, 1994.

[10] F. Y. Chuang, C. Y. Sun, H. F. Cheng, C. M. Huang, and I. N. Lin, "Enhancement of electron emission efficiency of Mo tips by diamond-like carbon coatings," *Appl. Phys. Lett.*, vol. 68, no. 12, p. 1666, 1996.

[11] K. C. Park, J. H. Moon, J. Jang, and M. H. Oh, "Deposition of hydrogen-free diamond-like carbon film by plasma enhanced chemical vapor deposition," *Appl. Phys. Lett.*, vol. 68, no. 25, p. 3594, 1996.

[12] Y. Shimada, N. Mutsukura, and Y. Machi, "Analysis of diamond phase in hydrogenated hard carbon film using radio frequency plasma etching," *J. Appl. Phys.*, vol. 71, no. 8 p. 4019, 1992.

[13] K. Nakazawa, S. Ueda, M. Kumeda, A. Morimoto, and T. Shimizu, "NMR and IR studies on hydrogenated amorphous Si1-xCx films," *Jpn. J. Appl. Phys.*, vol. 21, no. 3, p. L617, 1992.

[14] J. Tauc, *Amorphous and Liquid Semiconductor*, J. Tauc, Ed. London, U.K.: Plenum, 1974, p. 15.

[15] N. Mutsukura, S. Inoue, and Y. Machi, "Deposition mechanism of hydrogenated hard-carbon films in a CH_4 rf discharge plasma," *J. Appl. Phys.*, vol. 71, no. 1, p. 43, 1992.

[16] J. Robertson and E. P. O'Reilly, "Electronic and atomic structure of amorphous carbon," *Phys. Rev. B, Condens. Matter*, vol. 35, no. 6, p. 2946, 1987.

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