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# Field emission from hydrogen-free DLC

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**Abstract** – We have studied the field emission characteristics of diamond-like-carbon (DLC) films deposited by a layer-by-layer technique using plasma enhanced chemical vapor deposition, in which the deposition of a thin layer of DLC and a $CF_4$ plasma exposure on its surface were carried out alternatively. The hydrogen-free DLC can be deposited by $CF_4$ plasma exposure for 140 sec on a 5 nm DLC layer. $N_2$ gas-phase doping in the $CH_4$ plasma was also carried out to reduce the work function of the DLC. The optimum $[N_2]/[CH_4]$ flow rate ratio was found to be 9% for the efficient electron emission, at which the onset-field was 7.2 V/μm. It was found that the hydrogen-free DLC has a stable electron emitting property.

**key words:** DLC, hydrogen-free DLC, PECVD, layer-by-layer, field emission, FED, emission stability

## I. Introduction

Recently, field emission display (FED) has attracted much attention due to its unique properties such as wide viewing angle, wide operation temperature range, low power consumption and high brightness [1]. They are a viable alternative to AMLCD for several applications, where operating temperature and high ambient brightness are a problem. FED is not a new idea and one of its main attractions is that it works in essentially the same way as does the cathode ray tube - the source of electrons in the FED being conventionally an array of sharp emitting tips made of Si, W or Mo. The erosion and poisoning of these tips during operation have led to lifetime problems. An alternative is to use low electron affinity materials to produce flat cathode emitters with stable emission and long lifetimes and possibly to obviate the need for complex manufacturing techniques to produce the tips. DLC has become an attractive material for such an application.

Diamond-like carbon has unique properties such as high hardness, high thermal conductivity, low electron affinity, high transmittance, etc. These unique properties make it suitable for the cold cathode material for field emission display [2, 3]. N-doping in DLC reduces the work function of DLC and improve the electron field emission properties [4].

In this paper, we report on the deposition of hydrogen-free DLC by a layer-by-layer deposition technique [5-7] and electron emission behaviors of the hydrogen-free DLC and nitrogen doped DLC films. We will also report the field emission characteristics of the nitrogen gas-phase doped, hydrogen-free diamond-like carbon (DLC) films.

## II. Experiment

In this work, a layer-by-layer deposition method was applied to deposit the DLC films with various hydrogen contents. We used a conventional PECVD system, in which rf power was applied to the substrate holder. The $N_2/CH_4/H_2/He$ and $CF_4/He$ gas mixtures were introduced for the deposition of DLC layer and the surface treatment, respectively [8]. Glass plate and silicon wafer were used as the substrates for film deposition. The thin DLC layer was exposed to a $CF_4$ plasma because the $CF_4$ plasma removes weak bonds such as amorphous graphite and hydrocarbon phase. The $CF_4$ plasma exposure time is an important deposition variable to control the hydrogen content in the DLC. We fixed each layer thickness to 5 nm and varied the $CF_4$ plasma exposure time. Current-electric field (I-E) characteristics were measured between two parallel plates in vacuum of $10^{-7}$ Torr to characterize electron emission properties.

We deposited about 200 nm thick DLC films in order to measure the absorption of C-$H_n$ stretch modes by FT-IR (Fourier Transform Infrared spectrophotometry). The absorption coefficients corresponding to C-$H_n$ (n = 1, 2, 3) stretch modes and the hydrogen content from the integration of the absorption coefficients [9] were obtained. The inter-band optical absorption coefficients were measured using Perkin-Elmer UV-VIS-IR spectrophotometer and the optical band gap was obtained using Tauc s plot [10].

The $N_2$ was mixed in $CH_4$ plasma for the deposition of doped DLC films. Table 1 depicts the layer-by-layer deposition conditions for the nitrogen doped DLC. The flow rates of He, $H_2$, $CH_4$ were fixed at 20, 6 and 3 sccm, respectively. And $[N_2]/[CH_4]$ flow rate ratio was changed from 3 to 50% by varying $N_2$ flow rate. The $CF_4$ flow rate and $CF_4$ plasma exposure time were fixed at 20 sccm and 140 sec, respectively, for the plasma treatment. The measured self-bias voltage was found to be −120 V at a fixed rf power of 100 W. The self-bias voltage depends strongly on the gas pressure and on the rf power.

When considering the possible use of hydrogen-free DLC as a cold cathode material of field emission displays, the control of the Fermi energy through the band gap by doping and the stability of the material under bias-induced stress are very important. So, we studied the stability of the electron emission currents under bias-induced stress for the DLC and the hydrogen-free DLC.

**Table 1.** Layer-by-layer deposition condition for the DLC and N-doped DLC films

| Condition | DLC Deposition | N-doped DLC Deposition | $CF_4$ plasma exposure |
|---|---|---|---|
| RF power (W) | 100 | 100 | 100 |
| Pressure (mbar) | 0.4 | 0.4 | 0.45 |
| Flow rate (sccm) | | | |
| He | 20 | 20 | 20 |
| $H_2$ | 6 | 6 | 0 |
| $N_2$ | 0 | 0.09~1.5 | 0 |
| $CH_4$ | 3 | 3 | 0 |
| $CF_4$ | 0 | 0 | 20 |
| Sub. Temp. (K) | 300 | 300 | 300 |
| Time (sec) | 95 | 95 | 140 |

The hydrogen containing DLC and hydrogen-free DLC were bias-stressed in an electric field giving an emission current of 2~4 μA from the area of 0.5 $cm^2$. The current-electric field (I-E) measurements were performed with a scanning speed of 10 V/s from 0 to 32 V/μm.

## III. Results and Discussion

Figure 1 shows the absorption coefficients of C-$H_n$ stretching modes for the DLC films with $CF_4$ plasma exposure times of (a) 0s, (b) 50s, (c) 100s and (d) 120s, deposited using a layer-by-layer technique. The IR absorption peaks at 2925, 2960, and 2850 $cm^{-1}$ corresponding respectively to $sp^2$ asymmetry $CH_2$, $sp^3$ asymmetry $CH_3$, and $sp^3$ symmetry $CH_2$ stretch vibrations can be seen. The absorption band for $sp^2$ stretching modes appears at >3000 $cm^{-1}$, for example olefinic and CH aromatic rings appear at 3000 and 3050 $cm^{-1}$, respectively. In general, overall C-$H_n$ absorption coefficients decrease with increasing $CF_4$ plasma exposure time. However, as can be seen from Figs. 1(a) through (d), most of the hydrogen atoms bonded to $sp^2$ C-$H_n$ are

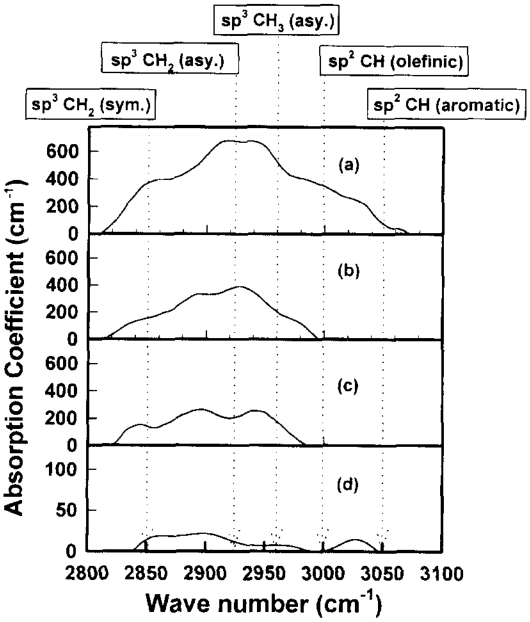

**Fig. 1.** Absorption coefficients of layer-by-layer deposited DLC films with various $CF_4$ plasma exposure times of (a) 0 sec, (b) 50 sec, (c) 100 sec and (d) 120 sec.

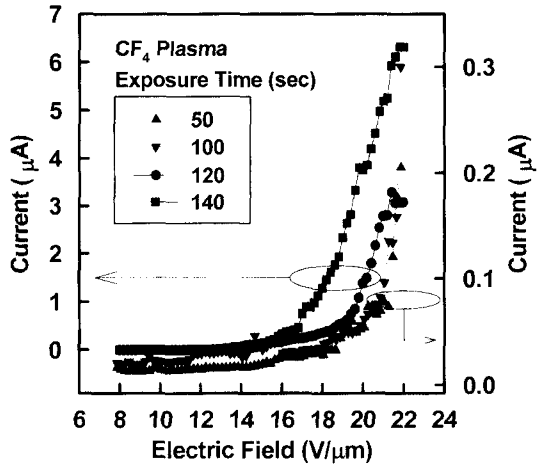

Fig. 2. *I-E* characteristics of the DLC films with various $CF_4$ plasma exposure times.

diffused out first and then hydrogen atoms bonded to $sp^3$ $C\text{-}H_n$ are desorbed.

Figure 2 shows the current (I) - electric field (E) characteristics of the 90 nm thick DLC on $p^+$ c-Si wafer, showing typical current emission behavior. It is noted that the emission current is the highest when $CF_4$ exposure time is 140s. From the comparison between the I-E characteristics of hydrogen-free DLC shown in Fig. 2 and hydrogen content of the DLC shown in Fig. 1, it is noted that the emission current increased rapidly when the H atoms were almost completely removed from the DLC film. Specially, after $CF_4$ plasma treatment longer than 120 sec, shown in Fig. 1 and Fig. 2, we could remove the large portion of hydrogen content and get higher emission current. Therefore the emission current is very high when the hydrogen atoms are almost completely removed from the DLC by $CF_4$ plasma exposure. It is important to have hydrogen free DLC for the efficient emission, which is the purpose of the layer-by-layer deposition technique.

Figure 3 shows the I-E characteristics of the hydrogen-free DLC after bias-induced stress under a field of 17 V/μm with various stress time. The $CF_4$ plasma exposure time was 140 sec to produce hydrogen-free DLC film. The emission current of the hydrogen-free DLC increases at first with bias-stress time and then stabilizes.

The average emission current of the hydrogen-free DLC increased up to 21600 sec and then saturated. In addition, it shows a little fluctuation of currents after bias-induced stress for a long time.

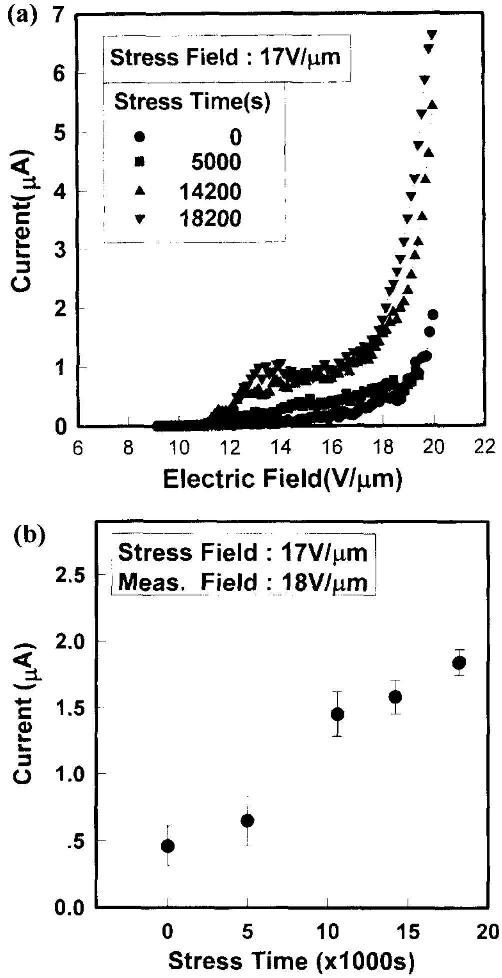

Fig. 3. (a) The *I-E* characteristics of the hydrogen-free DLC film with various bias-stress times and (b)current fluctuation under a field of 18 V/μm after bias-induced stress experiment under a field of 17 V/μm with various stress time.

The electron emission characteristics of the hydrogen-containing DLC and the hydrogen-free DLC have different behavior. The hydrogen-containing DLC showed unstable electron emission characteristics. It is noted that hydrogen content in the hydrogen-free DLC is less than 1 at.%. The $C\text{-}H_n$ bond strength is weaker than the C-C bond, which results in the easier bond breaking of the $C\text{-}H_n$ by carrier injection into the DLC. The hydrogen atoms are able to move in the network under the

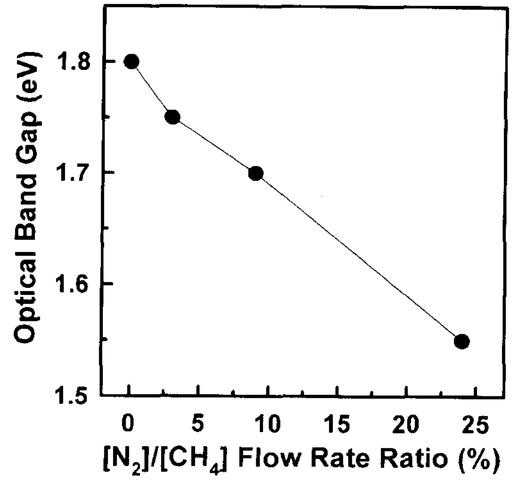

**Fig. 4.** The optical bad gap of the N-doped DLC films, in which DLC was deposited by a layer-by-layer technique with a $CF_4$ plasma exposure time of 140 sec.

electric field and cause unstable electron emission. However, the hydrogen-free DLC has stable electron emission characteristics because of the lower H incorporation. The current-induced changes of the DLC will be studied further in order to clarify the origin of the changes.

Figure 4 shows the optical band gap ($E_g^{opt}$) obtained from Tauc's plot for the DLC films. It decreases from 1.8 eV to 1.55 eV with increasing $[N_2]/[CH_4]$ ratio from 0 to 25 %. The decrease of optical band gap appears to be due to the increase of graphite phase in the DLC by nitrogen incorporation, as is the case for ta-C.

Figure 5 shows the I-E characteristics of the nitrogen doped DLC films. The electron emission current increases at first with $[N_2]/[CH_4]$ ratio up to 9% and then it decreases with further increase of $[N_2]/[CH_4]$ ratio. It may be related to the increase of graphite phase and carbon-nitrogen alloy in the DLC by nitrogen incorporation[11]. The optimum $[N_2]/[CH_4]$ ratio appears to be 9%.

Figure 6 shows I-E characteristics for the 9% gas-phase N doped DLC film measured before and after 10 hours of bias-induced stress at 10 V/μm. After 10h bias-stress at 10 V/μm, the emission current is much stabilized, which may be due to the improved contact between the DLC and Si wafer. The newly developed hydrogen-free, N doped DLC film appears to be a promising material for field emission because of its large area deposition capability and stable electron emission behavior. When considering the possible use of DLC as a cold cathode material, the control of the Fermi energy through the band gap by doping should be done to reduce its work function. The work function is related to the turn-on field for electron emission.

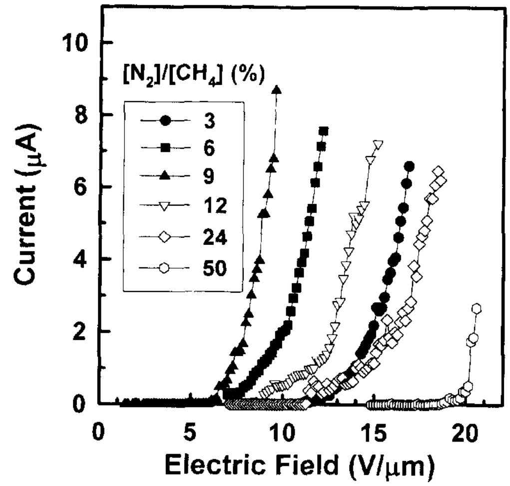

**Fig. 5.** *I-E* characteristics of the N-doped DLC films.

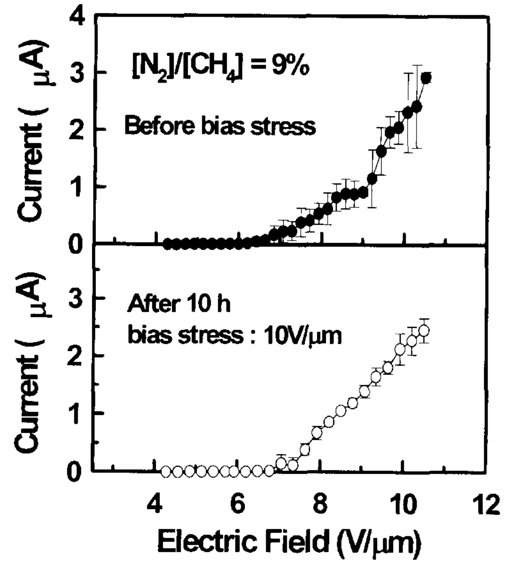

**Fig. 6.** *I-E* characteristics for the 9% gas-phase N-doped DLC film measured before and after bias-induced stress experiment at 10 V/μm for 10 hours.

Figure 7 shows the AFM(Atomic force micros-

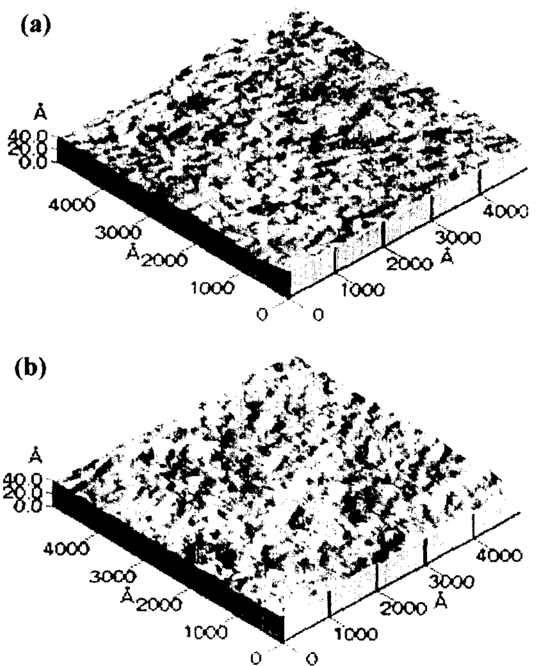

**Fig. 7.** AFM images of hydrogen-free DLC (a)before and (b)after the bias-induced stress experiment.

copy) image of the 9% gas-phase N doped DLC before and after bias-induced stress experiment for 10 hours. The surface of the DLC did not change after 10h bias-induced stress experiment, which was confirmed from scanning electron micrograph, atomic force microscope and Raman scattering analysis. But some microscopic change can be possible after bias-stress. Therefore, we conclude that the emission current increase was not due to the change of the surface morphology or the carbon bonding configuration.

## IV. Conclusion

The hydrogen-free DLC films deposited using a layer-by-layer technique have been developed and their emission behaviors have been studied. The emission current increases with decreasing hydrogen content in the DLC. It is noted that the emission current is high when the hydrogen atoms are almost completely removed from the DLC. The electron emission characteristics of the hydrogen-free DLC films were compared. The emission current of the hydrogen-free DLC increased at first and then stabilized. The instability of electron emission current appears to be related to the incorporated hydrogen. The hydrogen-free DLC showed the stable electron emission and enhanced electron emission current after bias-stress.

The electron emission behavior of gas phase nitrogen doped DLC films with various $[N_2]/[CH_4]$ flow rate ratios has been studied. The emission current density and onset field are strongly related to the gas-phase doping concentration in the DLC films. The optimum $[N_2]/[CH_4]$ flow rate ratio for efficient electron emission was found to be 9%. The onset-field and effective barrier energy for electron emission at 9% are 7.2 V/μm and 0.02 eV, respectively. The electron emission characteristics for the N doped hydrogen-free DLC were found to be quite stable after bias-stress.

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