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Field Emission Properties of Nano-DLC Films Prepared on Cu Substrates by Pulsed Laser Deposition

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Abstract: Nano-diamond like carbon (DLC) thin films were prepared on fused silica and Cu substrates by the pulsed-laser deposition technique with different laser intensities. Step-measurement, atomic force microscope (AFM), UV-VIS-NIR transmittance spectroscopy and Raman spectroscopy were used to characterize the films. It was shown that the deposition rate increases with the laser intensity, and the films prepared under different laser intensities show different transparency. Raman measurement showed that the content of sp^3 of the Nano-DLC thin films decreases with the laser intensity. The field emission properties of the Nano-DLC thin films on Cu substrates were studied by the conventional diode method, which showed that the turn-on field increases and the current density decreases with sp^3 content in the films. A lower turn-on field of 6 V/um and a higher current density of 1 uA/cm^2 were obtained for Nano-DLC thin films on Cu substrate.

Key words: nano-DLC thin films; pulsed-laser deposition; field emission properties

1 Introduction

Electron field emission from carbon-related materials, such as diamond-like carbon (DLC) films, amorphous carbon films, hydrogenated amorphous carbon films *etc*., has been received considerable attention for flat panel display in the microelectronic devices for their low surface work function[1]. In these materials, the DLC thin films show high wear resistance, low friction coefficient, surface smoothness and optical transparency. The difference in the properties of DLC thin films principally results from the different bonding configuration. The different content of sp^3, sp^2, and sp hybridized carbon plays an important pole in the chemical and physical properties of DLC thin film. Over the last years, special attention has been paid to preparing DLC films and controlling the sp^3, sp^2, and sp contents by various deposition methods[2,3] such as magnetron sputtering, chemical vapor deposition, *etc*. Among these methods, pulsed-laser deposition (PLD) shows excellent properties to grow ultrasmooth Nano-DLC thin films with high sp^3 content[4,5]. In order to improve the field emission properties, *n*-type impurities, such as P, Cu, Au, Ag, and N have been introduced into DLC thin films. These dopants can provide electrons to the conduction band of DLC thin films[6,7]. On the other hand, the kinds of substrates may also be an important factor that can improve the field emission properties of DLC thin films. A kind of good substrate can provide electron to the conduction band more than impurities because only a little content of the *n*-type impurities can doped in the DLC films. Until now, there are few reports about the field emission properties of Nano-DLC thin films on Cu substrates.

In this work, Nano-DLC thin films were prepared on fused silica and Cu substrates by PLD methods under different laser intensities. Atomic force microscopy (AFM), UV-VIS-NIR transmittance spectroscopy and Raman spectroscopy were used to characterize the films. The field emission properties of the Nano-DLC thin films on Cu substrates were studied by the conventional diode method

2 Experimental

Nano-DLC thin films were prepared by the PLD technique using a KrF excimer laser (λ=248 nm, τ=25 ns, and repetition rate=10 Hz). The focused laser beam is incident at an angle of 45^o on a pyrolitic graphite target

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(5 N purity). The target has a rotational and translational motion to ensure a uniform erosion pattern over the target surface. The laser intensity was varied between 5 and 17 J/cm^2. The fused silicon and Cu were used as the substrates. In order to avoid contamination of the films, the chamber was evacuated to a base pressure of 1.2×10^{-6} Pa. Some other experimental parameters are listed in Table 1. The deposition time was constant (60 min) for all the samples.

Thickness and surface morphologies of the films were determined by step-measurement and atomic force microscopy (AFM). The optical transmittance spectrum was obtained by UV-VIS-NIR spectrophotometer for the Nano-DLC thin films on fused silica with a wavelength range of 190-2 500 nm at room temperature and the optical gap was measured by transmittance spectra. The visible Raman spectra of Nano-DLC thin films was also collected using an excitation light with the wavelength of 532 nm. The field emission properties of Nano-DLC thin films on Cu were tested by the conventional diode method at an ambient pressure of about 2×10^{-4} Pa. The stainless steel panel acted as anode and the Nano-DLC thin films served as cathode with the anode-cathode spacing of 200 μm.

3 Results and discussion

The thickness of the Nano-DLC thin films was determined by step-measurement and the thickness was 85, 115, 134, 152, and 166 nm for A1, A2, A3, A4, and A5, respectively. It is obvious that the deposition rate increased with laser intensity since the deposition time was constant for all the films. The thickness of Nano-DLC thin films on Cu substrate was a little thicker than that on silica substrate under the same laser intensity, which is shown in Table 2. Fig.1 exhibits the images of the Nano-DLC thin films on fused silica (for sample A series) and Cu (for sample B series) substrates deposited under different laser intensities. It can be seen that the Nano-DLC thin films prepared under different laser intensities show different color, and the films on fused silica were transparent.

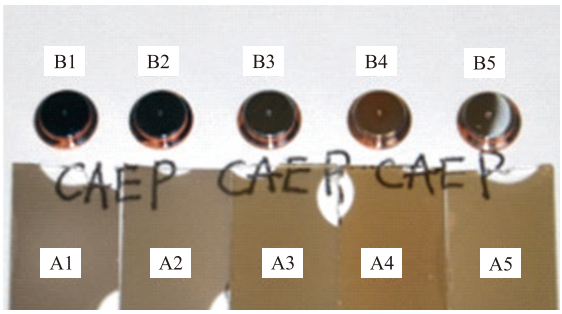

Fig.1 Images of Nano-DLC thin films on Cu (B series) and on silica (A series) substrate

The surface morphologies of the Nano-DLC thin films on Cu and on silica substrates were obtained by AFM, which are shown in Fig.2. The surface roughness (RMS) of the films is listed in Table 2. It is shown that the surface of the Nano-DLC thin films on fused silica is very smooth, which exhibits a small roughness of less than 1nm. The films on Cu substrates show large roughness of more than 7 nm. The reason is that the surface roughness of Cu substrate is about 5 nm, while that of fused silica is less than 1nm. The results demonstrate that the quality of substrates plays an important role for the surface morphology of Nano-DLC thin films.

Raman excited by visible light of DLC thin films is only sensitive to the sp^2 site due to its much greater scattering cross-section[10]. The spectra typically have two main peaks, the D peak around 1 350 cm^{-1} and the G peak around 1 580 cm^{-1}, which correspond to the

Table 1 Some main experimental parameters of Nano-DLC thin films

Sample	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
Substrate	Silica	Silica	Silica	Silica	Silica	Cu	Cu	Cu	Cu	Cu
Distance between target and substrate/mm	50	50	50	50	50	48	48	48	48	48
Laser intensity (J/cm^2)	5	8	11	14	17	5	8	11	14	17

Table 2 Some properties of Nano-DLC thin films

Samples	A1	A2	A3	A4	A5	B1	B2	B3	B4	B5
Thickness/nm	85	115	134	152	166	92	120	138	150	158
RMS (By AFM)/nm	0.98	0.72	0.51	0.47	0.63	9.4	7.1	8.7	8.5	9.3
Transmittance (%) @ 650 nm	43	38	35	39	41					
The optical band gap/eV	2.67	2.25	2.12	1.81	1.70					
sp^2/sp^3						0.45	0.51	0.56	0.57	0.56

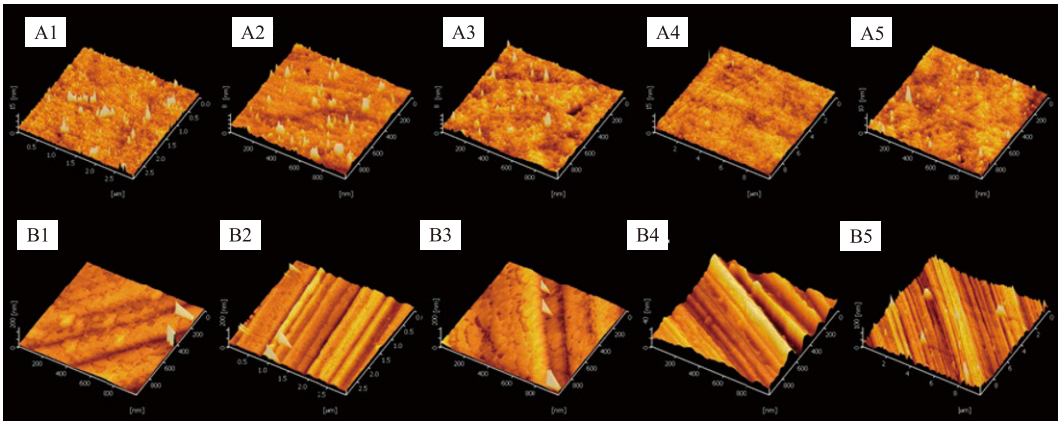

Fig.2 AFM surface morphologies of Nano-DLC thin films for A1-A5 on silica substrates, and B1-B5 on Cu substrates

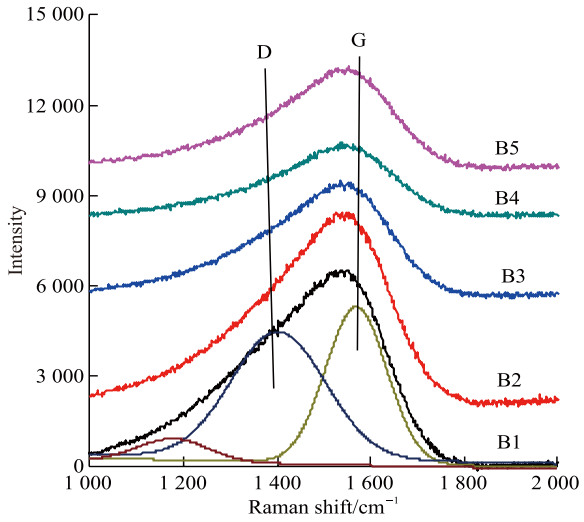

Fig.3 Visible (532 nm) Raman spectra of Nano-DLC thin films on Cu substrates

breathing mode of the aromatic rings and the stretching mode of the pairs of sp^2 sites in the aromatic rings or olefinic chains[8,9]. The parameters of Raman spectra such as position, widths and intensities of the D peak and G peak are closely related to the density, size, and structure of the sp^2 clusters. The properties of sp^2 clusters are in turn closely related to the sp^3 content of DLC, enabling us to measure the sp^3 content from the Raman spectra[10]. Fig.3 shows the Raman spectra of Nano-DLC thin films on Cu substrates. The Raman spectra were first treated with linear background removal and then fitted with two Gaussian peaks, simulating the D and G peaks. The D peak position shifts from 1 391.5 to 1 384.2 cm^{-1} with increasing laser intensity. Liu et. al observed the down-shift of D peak for DLC thin films and they proposed that the reason comes from the size of sp^2 cluster[11]. The G peak position exhibits a little high-shift (1 572.8→1 578.2 cm^{-1}), revealing only a small structural change in Nano-DLC thin films[12]. The ratio of sp^2 and sp^3 in the films can be deduced by the intensity ratio of the D and G peaks (I_D/I_G)[13,14], and the results are listed in Table 2. It is clear that the I_D/I_G ratio decreases with increasing laser intensity. Since smaller values of I_D/I_G ratio correspond to higher sp^3 content, the sp^3 content decreases with increasing laser intensity. It can be deduced that diamond-like carbon decreases with increasing laser intensity and higher laser intensity can make amorphous carbon transform from diamond-like structure to graphite-like structure.

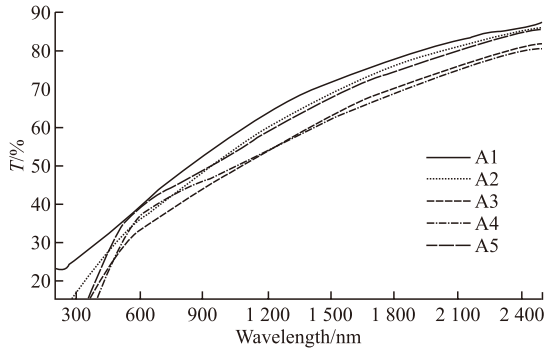

Fig.4 Transmittance spectra of Nano-DLC thin films on silicon substrate prepared at various powers

The UV-VIS-NIR transmittance spectra ranged from 190 to 2500 nm of the Nano-DLC thin films on fused silica prepared with different laser intensities are shown in Fig.4. It can be seen that the Nano-DLC thin films show low transmittance in the UV and visible range. With increasing laser intensity, the transmittance shows slight decrease, and then a slight increase in the visible range. The transmittance of the Nano-DLC thin films prepared under different laser intensities at 650 nm is shown in Table 2. We proposed that there are two reasons responsible for the change in the transparency of the Nano-DLC thin films. First, the thickness of the films increases with increasing laser intensity, which will reduce the transparency. Secondly, graphitic carbon increases and the diamond carbon decreases with laser intensity, which can be concluded from the Ra-

man spectra. It is obvious that graphitic carbon exhibits less transparency than diamond carbon.

The absorption coefficient of films can be calculated by using the following equation:

$$\alpha = \frac{ln(1/T)}{d} \quad (1)$$

where, α is the absorption coefficient and d is the film thickness.

For DLC thin films, the optical band-gap E_g on the absorption coefficient is given by the Tauc equation[15,16]:

$$(\alpha hv)^{\frac{1}{2}} = \beta (hv - E_g) \quad (2)$$

where, hv is the photo energy, α is the absorption coefficient, and β is a constant. The plot of $(\alpha hv)^{1/2}$ versus hv of the Nano-DLC thin films is shown in Fig.5, from which the band gap of the films can be obtained by extrapolating the linear portion. The band gap of the Nano-DLC thin films is in the range of 1.7-2.7 eV, and is shown in Table 2. It can be seen that the band gap decreases with increasing laser intensity. The reason may be that the sp^3 content in the films decreases with increasing laser intensity, and larger sp^3 content deduces a larger band gap. This result is in agreement with other report[17].

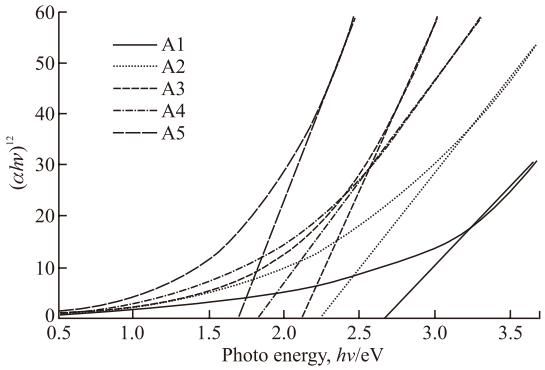

Fig.5 Plot of $(\alpha hv)^{1/2}$ versus hv of the Nano-DLC thin films on silicon substrate prepared at various powers

Fig.6 shows the field emission current density versus electric field (J-E) curves of Nano-DLC thin films on Cu substrate prepared under different laser intensities. In this work, the turn-on fields of the Nano-DLC thin films on Cu substrate to produce the current density of 1 μA/cm^2 are 8.9, 7.8, 6.4, and 6.0 V/μm for B1, B2, B3, and B4 respectively, which is evident that the turn-on field decreases sharply with increasing laser intensity. Under the same applied electric field, the emission current density increases with increasing laser intensity. The Raman spectra display that the content of sp^3 in the films decreases with increasing laser intensity, which means that the turn-on field increases with increasing sp^3 content in the films. A similar result was found by M. Shakerzadeh *et al* that a larger content of sp^3 in the films reduces the turn-on field for carbon films when they studied the field emission enhancement of carbon films by single pulse laser irradiation[18]. The reason is that the conductivity of sp^3 carbon is relatively poor, which limits its field emission, while the sp^2 carbon shows good conductivity, which exhibits good field emission property. The optimized field emission property was obtained from sample B4, which presents a current density of 1 μA/cm^2 at an applied electric field of about 6 V/μm. Compared with many previous reports on doped DLC field emitters, this value is much lower[19,20]. But this value is much higher than the un-doped DLC thin films on highly p-doped Si substrate[21]. The reason may be that Cu substrate has more electrons, these electrons may reach the anode under the action of the electric field, thus improve the field emission properties of the DLC thin films. A similar result was found by Huang that amorphous carbon deposited on copper nanowires exhibits excellent field emission properties[22].

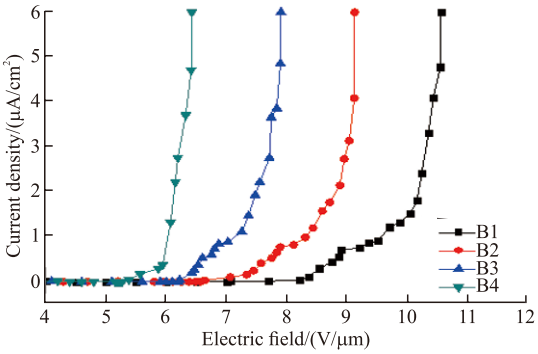

Fig.6 Field emission current density versus electric field (J-E) curves of Nano-DLC thin films on Cu substrate

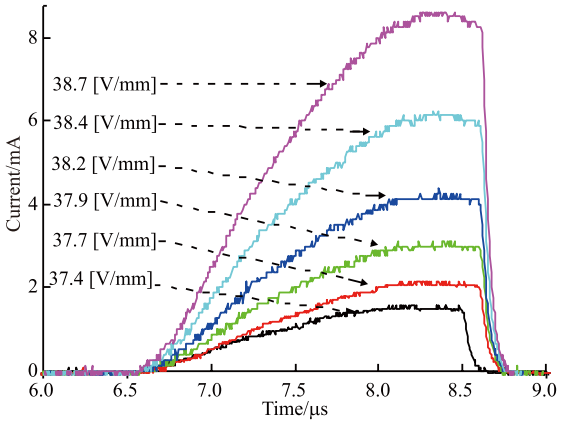

Fig.7 Emission current of Nano-DLC film (B2) withtime under different load voltage

In order to further study the field emission properties of Nano-DCL thin films, the sample B2 was put into an RF gun which can provide even higher electric field. The emission current under different load voltages with time is shown in Fig.7. Since it takes time to build the RF field in the gun, the emission current is increasing gradually at the beginning of the pulse. And when the RF field reaches a steady state, the emission current becomes constant as well. The maximum emission current density observed here is nearly 300 mA/cm^2.

4 Conclusions

Pyrolitic graphite target (5N purity) was used as target and fused silica and Cu were used as substrates to prepare Nano-DLC thin films by pulsed-laser deposition technique under different laser intensities. The deposition rate of the films increases with the laser intensity. The color of the films on Cu and on silica varies with the laser intensity. Transmittance measurement shows that all the films are transparent, and the optical band gap varies from 1.7 to 2.7 eV. Raman results show that less sp^3 content was obtained for the films deposited at higher laser intensity. The field emission properties of the Nano-DLC thin films on Cu substrates were studied by the conventional diode method and sp^2 rich sample shows good field emission properties. Excellent field emission performances of lower turn-on field of 6 V/um and higher current density of 1 μA/cm^2 were obtained. It was believed that Nano-DLC thin films on Cu substrate would have a potential advantage for field emission applications.

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