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Deposition of diamond-like carbon films by using liquid phase electrodeposition technique and its electron emission properties

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We have deposited diamond-like carbon (DLC) films by electrodeposition technique in methanol liquid. XPS showed the films mainly contain carbon. IR spectrum indicated that as-deposited films are hydrogenated carbon films, with the hydrogen mainly bonded to sp^3 carbon. Raman measurement suggested that the films consisted of sp^3 and sp^2 carbon. The field emission (FE) property of DLC coated on Si has been measured. The field emission of DLC films started at an applied voltage of 160 V, compared with silicon tip arrays at 600 V, and an emission current of DLC films up to 55 μA at 360 V was achieved.

1. Introduction

In recent years, electron field emission (FE) has become an area of great interest. To achieve this behavior at low applied voltage, one approach is to cover the cathodes with a thin layer of material of low work function, so that FE is obtained easily at low applied voltage. The diamond films are known to be good for FE [1–3] due to their negative electron affinity (NEA) [4–5], immunity to chemical attack, hardness and high thermal conductivity. Diamond films can be grown as a polycrystalline thin film over wide area by chemical vapor deposition (CVD). The FE from diamond films has recently been studied for application for field emission displays. However, CVD diamond requires a growth temperature above 700°C, which limited the application of many substrate materials. Moreover, the diamond crystal shape also affected the electron emission. Robertson [6] researched the NEA of diamond and suggested that the low electron affinity derives fundamentally from its electronic bonding, i.e. the electron affinity depends on the type of bonding, not the crystallinity. Hence, amorphous diamond-like carbon (DLC) film should be a suitable material for FE. And DLC film also has a low electron affinity, and can be deposited cheaply at lower temperature onto glass, plastic substrates and so on. Hence, research of FE properties for DLC films has significant scientific and technological implications.

DLC films are deposited mainly by using various of vapor phase methods. Using these techniques, high quality films and rapid growth rates have been achieved. However, deposition of DLC films in the liquid phase is seldom reported. 1992, Namba [7] first attempted to prepare diamond and DLC films from the liquid phase by using ethanol as electrolyte. No obvious evidence could be seen to confirm that diamond or DLC films were obtained. The liquid phase technique has attracted much interest during this time because of its low (and even room) deposition temperature [8–11]. Recently, we deposited successfully DLC films on conductive glass substrates using a pulse-modulated source in methanol liquid [12]. In this work, we deposited the DLC films on silicon tip arrays with the same method, analyzed the composition of films, and measured its electron FE. The details of the procedure and results are described below.

2. Experiment

2.1. The fabrication of silicon tip arrays

The arrays of silicon tips were fabricated using the method for creating silicon points by wet chemical etching [13]. The arrays were formed on (100) Si n-type wafers (resistivity is low 0.05 Ω m). The tip sharpening was performed by oxidation of the as-etched tips at 1050°C in dry oxygen. After the oxidation the oxide was removed in HF : H_2O solution. This sharpening technique allows production of tips with a radius of curvature of 10–20 nm. The arrays were 50 × 60, the bottom of the silicon tip was 7.5×7.5 μm^2, and the distance between the silicon tips was 25 μm.

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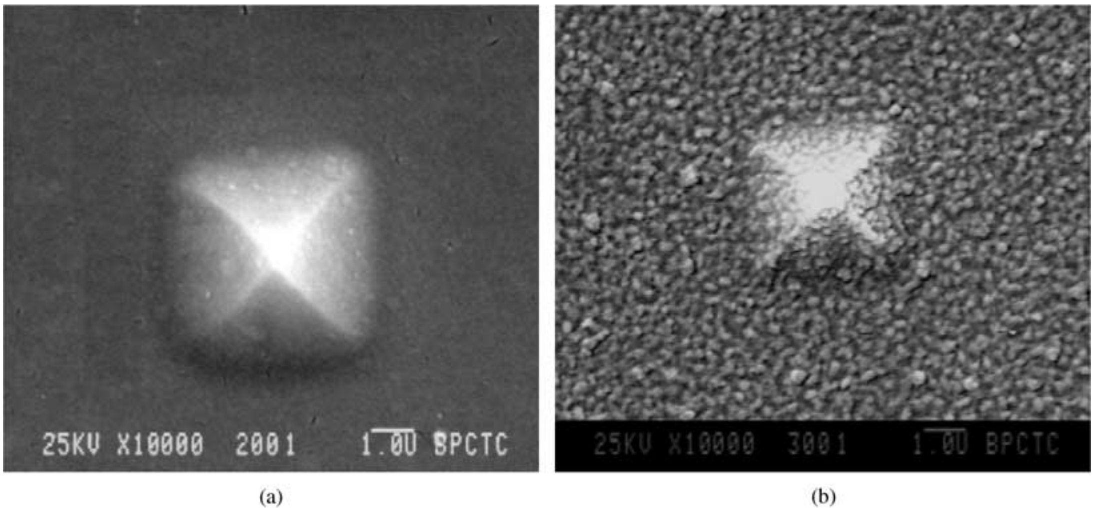

(a) (b)

Figure 1 The SEM images of single silicon tip before (a) and after (b) coated films.

2.2. The deposition of DLC films

The experimental setup has been described earlier [10, 12]. Analytically pure methanol (99.5%) was used as electrolyte. The silicon tip arrays sheet was mounted on the negative electrode. The distance between Si and the positive electrode (graphite) was set to 4 mm. The modulation potential applied to the substrate was 1000 V. The modulation duty cycle and modulation frequency were 50% and 7 kHz, respectively. The current density shifted up and down at about 0.2 mA/mm^2 in the deposition process.

The composition of the sample was characterized using a Perkin-Elmer PHI 5300 ESCA X-ray photoelectron spectroscope (XPS). A Perkin-Elmer (L-710) Fourier transform infrared (FTIR) spectrophotometer was used to study the C-H configurations. Raman measurements were obtained by using a Renishaw-1000 type confocal Raman spectrometer with 514.5 nm argon ion laser. The electrical resistivity was tested by a four-point probe method.

3. Results and discussion

The as-deposited films with pale color are transparent to infrared, and have high adhesion on Si substrates. The electric resistivity of the film was over 10^8 Ω cm. The hardness (DLC/Si) was more than 4500 kg/mm^2. In addition, the films have good chemical inertness in various corrosive chemicals.

Fig. 1 shows the SEM images of single silicon tip with (b) or without (a) films. From the figure, the silicon tips covered by irregular shape particles with dimension 100–300 nm, and no crystalline facets can be observed (Fig. 1b). The thickness of films is comprised of limited several layer particles. The composition of films was measured by XPS (Fig. 2a). The survey spectra indicated the film mainly consisted of the carbon band except for the oxygen band. The latter may originate from the contaminated oxygen in air or solution. The C1s spectra of the films are shown in Fig. 2b; it indicated that the binding energy (285.75 eV) is higher than the value in graphite (284.6 eV), which can be assigned to an amorphous carbon in DLC films. The tail to the high binding energy is related to the C-O [14, 15].

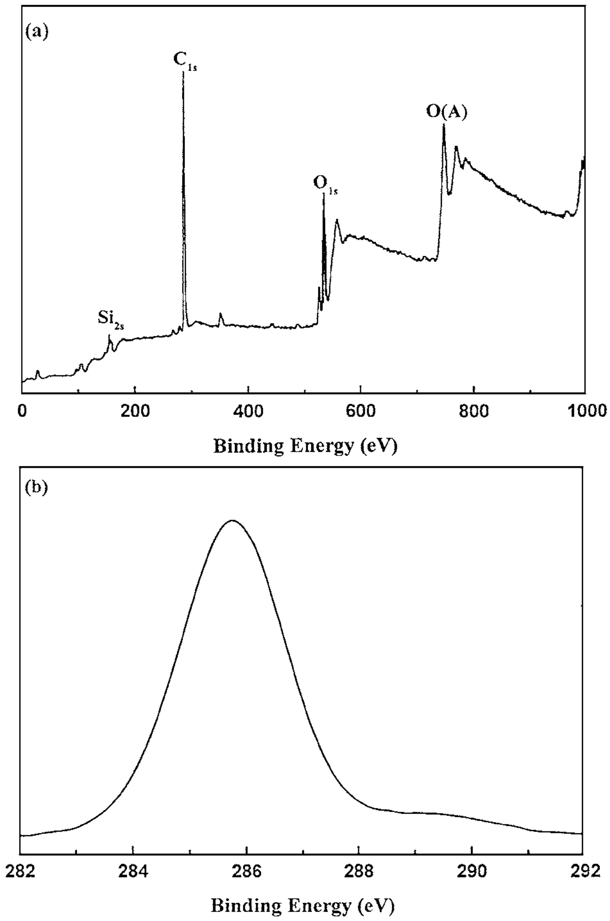

Figure 2 The XPS survey (a) and C1s spectra (b) of films coated on silicon tip arrays.

It is well known that the stretching C-H vibrations are rather sensitive to their environment, since IR absorption spectroscopy was particularly well suited as a probe of the different C-H configuration. Fig. 3 shows the IR spectra of films in the 2800~3000 cm^{-1} range. There were three obvious bands that could be observed: the bands at 2850 and 2920 cm^{-1} corresponded to the stretching vibration of sp^{3}CH$_3$ group; another weak band at 2960 cm^{-1} can be assigned to the stretching vibration of sp^{3}CH$_2$ group. However, the aromatic character corresponding to sp^{2}CH stretching vibration

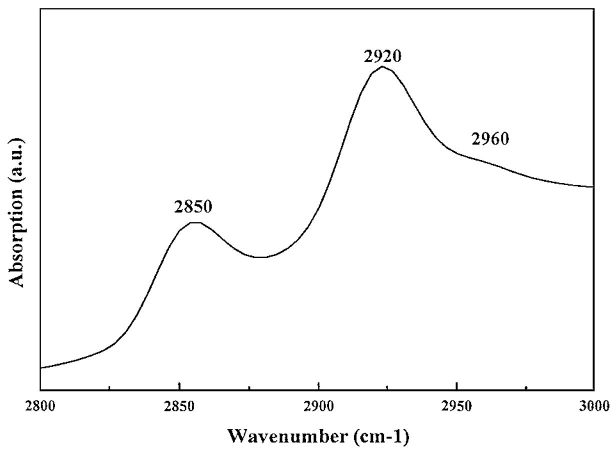

Figure 3 The IR spectra of films coated on silicon tip arrays.

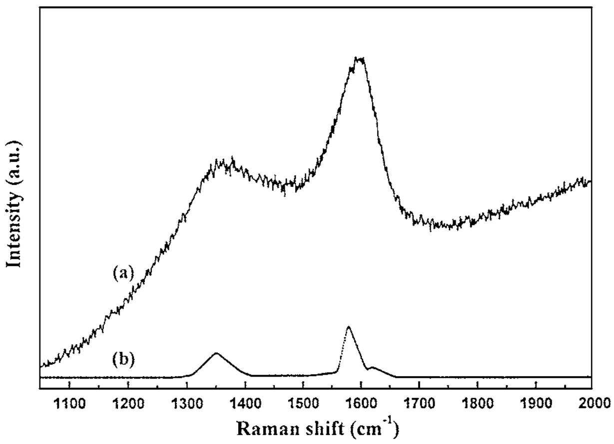

Figure 4 The Raman spectra of film deposited on silicon tips (a) and graphite (b).

around 2966~3050 cm^{-1} was very weak. The analysis showed that hydrogen bonds mainly to sp^3 CH.

Raman spectroscopy is a widely used technique to identify the bond and the structure of carbon-base materials. The first-order Raman spectrum of diamond consists of a single line at 1332 cm^{-1}. The corresponding spectrum of large single-crystal graphite also has a single high-frequency line at about 1580 cm^{-1}. Raman spectra for the amorphous carbon exhibit two broad peaks around 1200–1450 cm^{-1} for the D mode and 1500–1700 cm^{-1} for the G mode. The G band corresponds to graphite-like layers of sp^2 microdomains, while the D band is attributed to the bond-angle disorder in the sp^2 graphite-like microdomains induced by the linking with sp^3 carbon atoms as well as the finite crystalline sizes of sp^2 microdomains [16–18].

Fig. 4 displays Raman spectra of deposited film (a) and anode graphite (b). The characteristic Raman bands located at 1350 and 1580 cm^{-1} are narrow. The films' spectra are superposed on that of photoluminescence excited by an incident laser beam, which suggests that hydrogen may be contained in the film [19]. There are two asymmetric Raman bands centered at about 1600 and 1375 cm^{-1}, respectively. Comparing with the Raman spectrum of graphite, the line-width is much broader, which indicates that the films contain disordered phase. In general, the low frequency signals origin from the sp^3 carbon, the high-frequency signal is characteristic of sp^2 carbon. The Raman efficiency for sp^2 carbon bond is far larger than that of sp^3 carbon bond (approximately 50 times different). For the ratio of the peak height of sp^2 and sp^3 measurement from the PL spectrum, it can be concluded that sp^3 carbon bond is dominant in the film. The results suggested that the film is a mixture structure of sp^2 and sp^3 carbon. Combining the properties of the films, high resistivity and hardness, we suggest that the films are DLC. The silicon tip array coated with DLC film was placed in a high vacuum system which could be pumped to the stable pressure of 0.001 Pa. The emission current as a function of the anode voltage (I-V) was measured in a diode structure. The sample was used as the cathode and the silicon wafer as the anode. A 4 μm thick SiO_2 film was used as a spacer. Fig. 5 shows an I-V plot of the arrays with coated or not coated by DLC films. The FE of DLC films on silicon arrays started at 160 V voltage. Currents up to 55 μA were observed at the applied voltage of 360 V. It was confirmed that when the uncoated silicon tip arrays were placed instead of the arrays coated with DLC films, very small current could be observed until the applied voltage was above 600 V in the same vacuum system. Hence, it can be suggested that the FE efficiency can be enhanced in DLC film with an emission field only 40 V/μm. The mechanism of the emission from diamond films is not well understood. Analysis of the Fowler-Nordheim equation gives an effective work function of only 0.2 to 0.3 eV, compared to about 4.15 eV for silicon. Hence, most

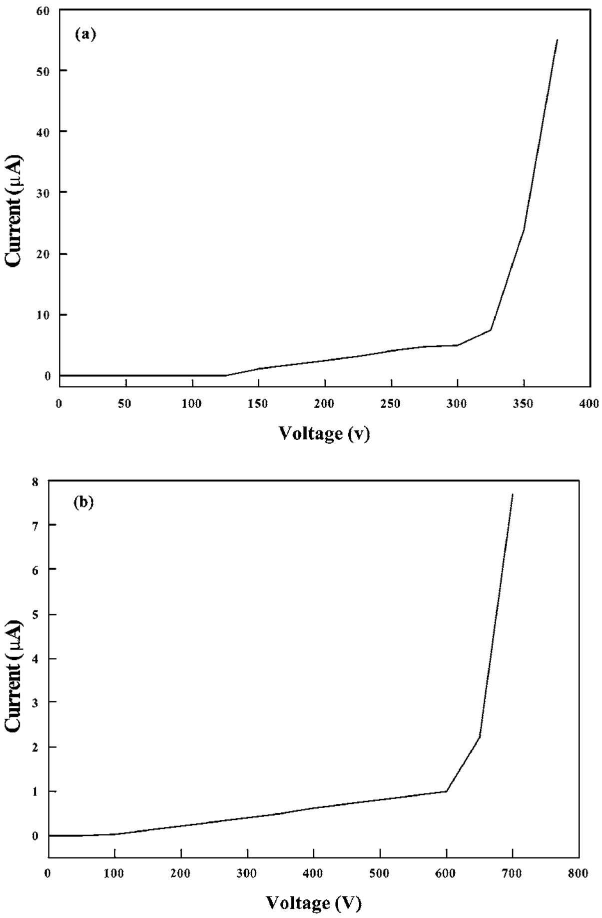

Figure 5 Emission current vs anode voltage (I-V) curve of films on silicon (a) and uncoated silicom arrays (b).

reports suggested that the low work function or NEA, along with the presence of graphite for providing electron conduction, play important roles in enhancement of emission efficiency [20–22]. It is noted that DLC films used for FE by Davis [23] also showed the electron emission could be attributed to the presence to both diamond and graphite carbon. Feng [24] researched the structure of DLC films with x-ray diffraction, electron energy loss spectroscopy, and Raman spectroscopy and suggested that the presence of carbon with a high degree of sp^3 bonding could induce significant electron emission. These results confirmed that component of sp^2 and sp^3 carbon present in carbon films can induce FE. The conditions appear to be present in our DLC films, which is a mixture of both sp^2 and sp^3 carbon. The structure is responsible for the electron emission.

Moreover, comparing to the emission field of $26\sim10$ V/μm for DLC films by CVD techniques [25, 26], the emission field of DLC films in the present test is still high. The liquid phase deposition is relatively simple and low cost, making it very attractive as a cost-effective process for FE of cathodes in microelectronics. So it is pursuing research further for the deposition of high quality DLC films.

4. Conclusion

Hydrogenated diamond-like carbon films with electrical resistivity above 10^8 Ω cm were deposited on silicon tip arrays in methanol using a pulse-modulated source. The structures of the films are characterized by XPS, Raman and IR spectroscopy, which indicated that the films consist of both sp^3 and sp^2 carbon. The emission field of DLC films started at 40 V/μm, and the current increased up to 55 μA at 90 V/μm. Comparing to the silicon tip arrays, the emission voltage is decreased strongly in the same test.

Acknowledgements

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