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# Field Emission from Amorphous carbon Nitride Films Deposited on silicon Tip Arrays *

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*Amorphous carbon nitride films (a-$CN_x$) were deposited on silicon tip arrays by rf magnetron sputtering in pure nitrogen atmosphere. The field emission property of carbon nitride films on Si tips was compared with that of carbon nitride on silicon wafer. The results show that field emission property of carbon nitride films deposited on silicon tips can be improved significantly in contrast with that on wafer. It can be explained that field emission is sensitive to the local curvature and geometry, thus silicon tips can effectively promote field emission property of a-$CN_x$ films. In addition, the films deposited on silicon tips have a smaller effective work function ($F = 0.024\,eV$) of electron field emission than that on silicon wafer ($F = 0.060\,eV$), which indicates a significant enhancement of the ability of electron field emission from a-$CN_x$ films.*

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carbon-based electron field emitters have attracted considerable attention due to possible applications in field emission devices. These carbon-based materials such as diamond, diamond-like carbon,[1,2] amorphous carbon,[3,4] and carbon nanotubes,[5,6] have been reported to show good electron field emission properties, i.e., emission at moderately low electric field. Electron field emission at low fields is mainly attributed to the low electron affinity of these carbon-based materials. So far, there have been a few reports on the electron field emission of carbon nitride films,[7−10] which exhibited a low threshold voltage and high emission current. In fact, early C-N studies focused primarily on its structure and mechanical characteristics, further in-depth studies of the $CN_x$ materials have been needed. It is well known that the a-$CN_x$ materials possess many desirable characteristics beyond its perfect mechanic characteristics such as stable chemical property and resistance to erosion as well as oxidization. More important, the a-$CN_x$ film has a wide band gap and negative electronic affinity. These characteristics of a-$CN_x$ films also make it possible that a-$CN_x$ materials can be used as the cold cathode under extreme conditions.

In this Letter, we investigate field emission properties of a-$CN_x$ films deposited on silicon tips by using magnetron sputtering in pure $N_2$ atmosphere. Silicon tips were selected as the substrate material because it may further improve the field emission properties of the films, which have been reported recently by a few group[11−13] using amorphous carbon coating silicon tips. However, there is little knowledge about the field emission from silicon tips coated by a-$CN_x$ films.

Amorphous carbon nitride films were deposited on silicon (001) tips and wafer substrate using rf magnetron sputtering high purity (99.99%) pyrolytic graphite (100 mm in diameter), respectively. Silicon tip arrays were prepared through oxidation, photo-etching, and chemical, etching. The height of silicon tips used here is about 3 $\mu$m and distance between tips is about 10 $\mu$m. Silicon wafer was cleaned by ultrasonic processing using ethanol and acetone. The chamber was evacuated by turbomolecular pump to less than $6.0\times10^{-4}$ Pa prior to film deposition. During the deposition, a-$CN_x$ films were synthesized simultaneously on silicon tips and wafer substrate in pure $N_2$ (99.99%) discharge, and nitrogen partial pressure was kept at 0.5 Pa, the rf power and the substrate temperature was kept to be constant at 150 W and 350 °C, respectively. The thickness of as-deposited film is about 180 nm. Other experimental details have been described elsewhere.[14]

The field emission measurements were performed in ultra high vacuum of $10^{-8}$ Pa. In the field emission testing, the a-$CN_x$ coating on silicon tips or wafer substrates was used as the cathode while an ITO coated glass plate was used as the anode. The distance between the anode and cathode was kept at 100 $\mu$m by inserting an insulation glass fibre between the anode and cathode. A high voltage was applied to the anode. The current meter integrated with a voltage supply was used for the current measurement. The voltage between the anode and the cathode was varied while the current was recorded simultaneously. In addition, the surface morphology of silicon tips was characterized using scanning electron microscopy

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(SEM). The chemical bonding state and composition of the films were analysed by Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS).

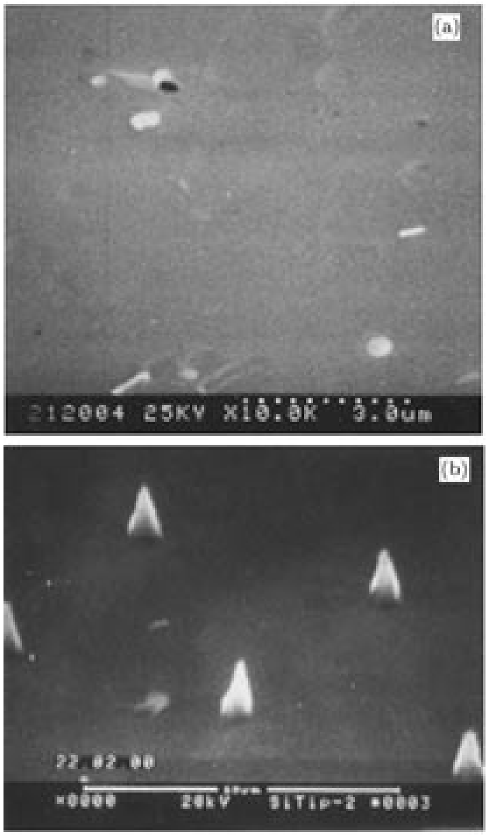

**Fig. 1.** SEM micrograph of silicon wafer (a) and tips (b) coated by a-CN$_x$ film.

The SEM image of silicon wafer and tips after a-CN$_x$ films coating are shown Fig. 1. The SEM of silicon wafer coated by a-CN$_x$ films does not show any obvious surface character. Whereas the SEM of silicon tips shows that the tips are sharp and uniformly arrayed. After coating, however, the apices of the tips became blunt slightly. The total geometry does not change from the original shape. The films are deposited very uniformly, showing a smooth surface morphology. The x-ray photoelectron spectroscopic technique is used to determine the composition of the films, and a typical spectrum is shown in Fig. 2. By measuring the areas under the spectral peaks, we estimate that the atomic content of the nitrogen in the films is about 32%, C and O atomic content is about 65% and 3%, respectively. A drastic decrease in the O content occurs after Ar$^+$, etching, indicating that most O atoms exist on the film surface. It is probably related to the incorporation of oxygen into the films while the film exposes to the atmosphere before the x-ray photo-electron spectroscopic (XPS) measurement. The FTIR spectrum of a typical a-CN$_x$ film deposited on a silicon wafer is shown in Fig. 3. The typical absorption of CN bonds such as C-N (1200–1300 cm$^{-1}$), C=N (1600–1700 cm$^{-1}$), C≡N bonds ($\sim$ 2200 cm$^{-1}$), G ($\sim$ 1550 cm$^{-1}$) and D band ($\sim$ 1350 cm$^{-1}$)[15] are detected in the FTIR spectrum for the as-deposited film. Except for C≡N bonds, the overlap of other bands causes broadening of absorption band between 1000 and 1700 cm$^{-1}$. This reveals that the as-deposited films are mainly composed of carbon and nitrogen bonded atoms in different chemical configurations.

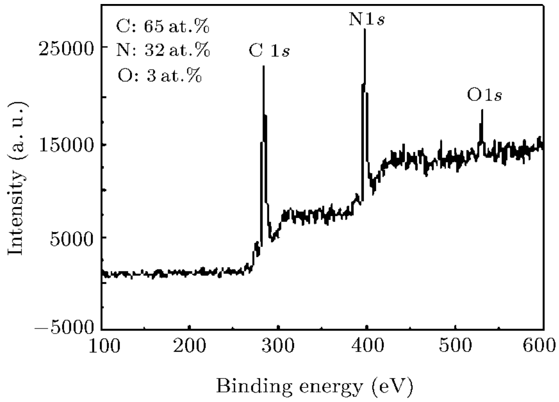

**Fig. 2.** Typical XPS spectrum of as-deposited a-CN$_x$ films.

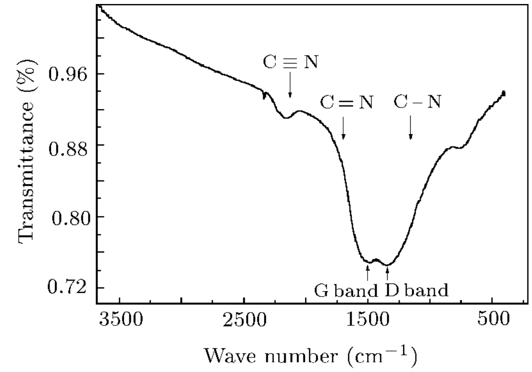

**Fig. 3.** Typical FTIR spectrum of as-deposited a-CN$_x$ films.

Figure 4(a) shows the field emission properties of the films on silicon tips and on silicon wafers, respectively, under the same deposition conditions. The a-CN$_x$ films deposited on silicon tips have better field emission properties than those on silicon wafers since the threshold voltage for the films on silicon tips is lower than that on silicon wafers. Correspondingly, the threshold voltage (500 V) of a-CN$_x$ films on silicon tips is much lower than that (1400 V) on the silicon wafers. It indicates that the field emission depends highly upon the geometry of the emitter. Because of the sensitivity of field emission to local curvature and geometry, the roughness in the film surface may be the controlling factor. The silicon tips are very sharp and uniform, which can geometrically enhance the electrical field. In contrast, when the field emitter is coated with carbon nitride the sharpness of the initial tips can be still maintained on condition that the coating is not too thick and the damage by ion bombardment during deposition is minimized.[16] On the other hand,

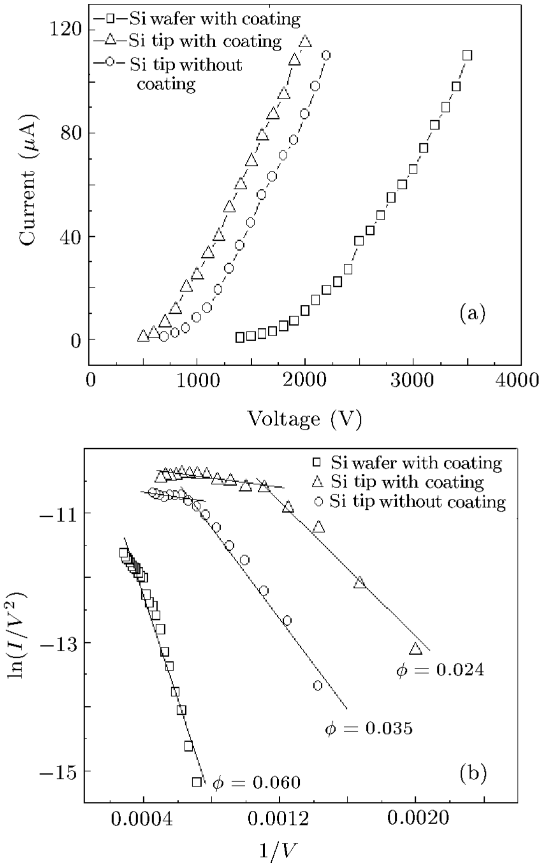

**Fig. 4.** The $V-I$ (a) and Fowler–Nordheim plots (b) of field emission properties for silicon wafer with coating, silicon tips with and without coating.

the effective work function is also an important factor to affect field emission of the films. Higher effective work function means that it is difficult for electrons to escape from the films; that is to say, the ability of electron field emission from the a-CN$_x$ films is lower. The effective work function of the films on silicon tips and wafer can be estimated by the Fowler–Nordheim (F-N) theory formula $I \propto (E^2/\Phi)\exp(B\Phi^{3/2}/E)$, where $\Phi$ is the efficient work function and $B$ is the constant $(6.84\times10^9)$. The results show that the effective work function of a-CN$_x$ films deposited on the silicon tips is 0.024 eV, which is smaller than that on the wafer of 0.060 eV. Since the electron field is concentrated on the silicon tips, the effective work function of the films will be reduced,[17] which is very favourable to improve the field emission of the films. In addition, Fig. 4(*a*) shows a comparison between field emissions from silicon tips with and without a-CN$_x$ coating. The threshold voltage of silicon tips with a-CN$_x$ coating decreased to 500 V from 700 V of the silicon tips without coating. Correspondingly, the effective work function of the films was also reduced from 0.035 eV to 0.024 eV. The emission current for silicon tips coated by the a-CN$_x$ films is significantly higher than that for silicon tips without any coating. It is very likely that the uniform and smooth coating of a-CN$_x$ films with a negative electron affinity (NEA)[9] is helpful in increasing the emission current of silicon tips.

Figure 4(b) displays the F-N plots of the a-CN$_x$ films deposited on silicon tip, silicon wafer and silicon tips without coating. The linear F-N characteristics of a-CN$_x$ film on the wafer indicate that its field emission is responsible for the acquired currents, which is consistent with the conventional F-N theory. However, the downward bending occurs in the F-N plots for a-CN$_x$ deposited on the tips and pure silicon tip without coating. This downward bending of F-N plots could be split into two sections, which can be fitted by two straight lines with different slopes. These two lines suggest that the current originates from two different types of emission sites,[18] which may be attributed to the fact that electron can emit from the tips but also from the sides.

In summary, a-CN$_x$ films with 32% N content are deposited on silicon tips and wafers using rf magnetron sputtering, respectively. The films on the tips show good electron field emission properties with a lower threshold voltage compared with the films deposited on the wafers. Silicon tips can decrease the effective work function of the films and geometrically promote to the electric field enhancement of a-CN$_x$ films. In addition, it has been found that the a-CN$_x$ films coating on the silicon tips can enhance significantly the field emission property of original silicon tips due to the NEA of a-CN$_x$ films. It is worth noting that the damage of silicon tips should be avoided during the deposition of carbon nitride films, or else, carbon nitride films on the tips cannot exhibit an excellent field emission property.

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