Enhancement of electron field emission property with silver incorporation into diamondlike carbon matrix

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Effects of silver doping on the electron field emission properties of diamondlike carbon films deposited on silicon substrates by the rf reactive sputtering technique were studied in detail. It was found that the threshold field and effective emission barrier were reduced by Ag doping and the emission current strongly depends on the Ag doping percentage. The threshold field was found to decrease from 6.8 to 2.6 V/μm with a variation of Ag at. % from 0 to 12.5. The field enhancement factor was calculated and we have explained the emission mechanism. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2926676]

Diamondlike carbon (DLC) film has been extensively studied during the past two decades due to their remarkable properties and potential applications. The properties and, subsequently, the quality of the DLC films strongly depend on their microstructure, which is commonly considered as an amorphous mixture of sp^2 and sp^3 hybridized carbon atoms.[1] The ratio of sp^2/sp^3 carbon atoms is one of the most important factors determining the quality of the DLC films, which can be changed by incorporating different metals or nonmetals into the DLC matrix. Various attempts have been made to dope amorphous DLC films with different elements and the doping effects of these elements have been extensively investigated in terms of the electrical, optical, and mechanical properties of DLC films.[2–9]

An enormous interest has been developed in the area of electron field emission property of DLC after the first direct study of field emission from a-C:H was performed by Amaratunga and Silva in 1996.[5] The advantages of DLC over diamond or carbon nanotube are its low temperature and large area uniform deposition, leading to the intensive study of field emission in DLC. The field emission properties of DLC films are mainly dependent on the variation of chemical bonding structure and the doping such as boron, phosphorus, nitrogen, sulfur, silicon, tin, etc., into the DLC matrix.[5–11] This doping increases electron field emission at low turn-on fields by raising their Fermi level and lowering the work function of the material. Ilie *et al.*[12] reported that the size of the sp^2 phase can dominate the effect on field emission of DLC since electron emission originates from the sp^2 phase in amorphous carbon (a-C) materials.[13] In this work, we have reported the effect of silver incorporation on the field emission properties of DLC films. The threshold field and field enhancement factor were calculated.

The silver incorporated diamondlike carbon (Ag:DLC) thin films were synthesized by the rf reactive sputtering technique at room temperature (300 K). The silicon substrates were cleaned by standard cleaning procedure before they were placed in the deposition chamber. To deposit the Ag:DLC thin films, the deposition chamber was evacuated to a base pressure of 2×10^{-6} mbar, and then methane (CH_4)

and argon (Ar) gases were introduced into the chamber for a fixed deposition pressure of 0.1 mbar. A rf power (13.56 MHz) supply was applied in the high purity (99.99%) Ag sputter target. For the variation of Ag concentration in the films, the ratio of methane to argon sputter gas and rf power has been changed from 80% to 40% and from 150 to 180 W, corresponding Ag at. % ranging from 0 to 12.5, respectively.

Composition of the films (Ag, C) were determined by energy dispersive x-ray analysis (Oxford, model 7582). The carbon and Ag bonding configuration and the sp^2/sp^3 ratio of the DLC films were determined by x-ray photoelectron spectroscopy (XPS) (PerkinElmer 1257). The surface morphology of the films was studied by a multimode atomic force microscope (SPM, Solver P47H-PRO). The microstructure of the Ag:DLC films was studied by a high resolution transmission electron microscope (HRTEM) (JEOL-JEM-2100). Field emission measurement was conducted in a high vacuum ($\sim 10^{-8}$ Torr) chamber. Indium tin oxide coated glass was used as an anode and placed above the Ag:DLC films. To characterize the emission behavior, a high-voltage supply and a multimeter remotely controlled by the computer interface are used.

Figure 1 shows the XPS C 1s (~ 284 eV) peaks of Ag:DLC films deposited with different Ag concentrations.
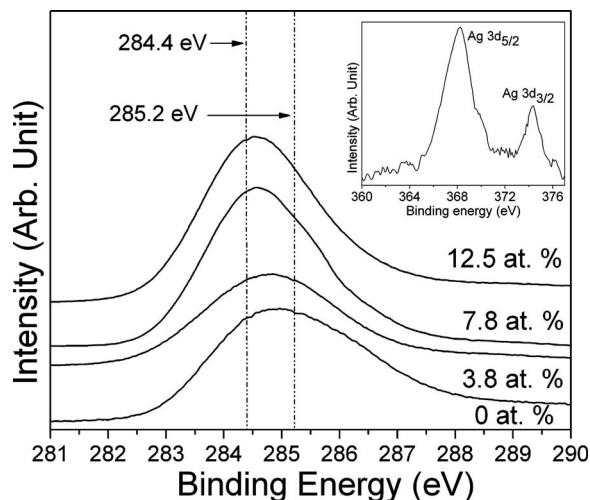

FIG. 1. XPS spectra of C 1s peak of DLC films for different at. % of Ag and the Ag core level spectra of 7.8 at. % Ag content DLC films in the inset.

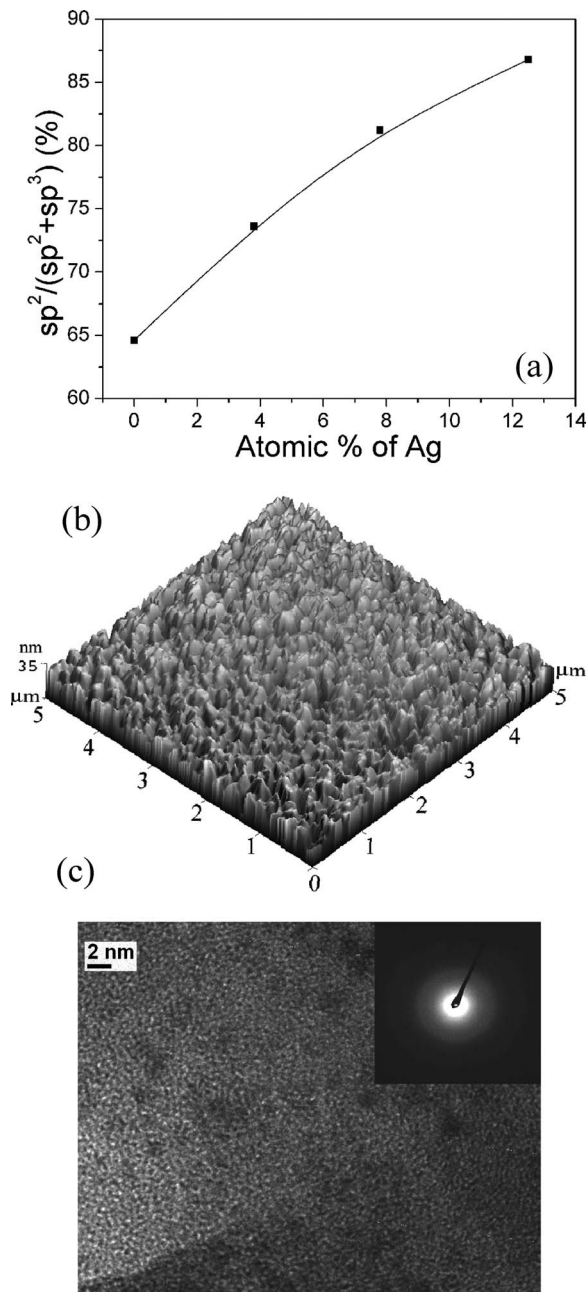[a]Author to whom correspondence should be addressed. Electronic mail: faruquekist@gmail.com.

FIG. 2. (a) Variation of $sp^2/(sp^2+sp^3)$ ratio with Ag at. % in the DLC films, (b) 3D AFM image, and (c) HRTEM images of 12.5% silver doped DLC film with the electron diffraction pattern at the inset.

FIG. 3. Emission current density (J) vs macroscopic field (E) curves of Ag:DLC films for different at. % of Ag and inset corresponding FN plot.

The core level XPS spectrum (inset of Fig. 1) of Ag 3d region consists of two binding energy peaks corresponding to Ag 3$d_{5/2}$ (368.2 eV) and 3$d_{3/2}$ (374.2 eV), respectively, which suggests that silver has been incorporated into the DLC matrix. Differences can be observed from the C 1s spectra (Fig. 1) acquired from the Ag:DLC films with different at. % of Ag. As the Ag at. % increases, the peak position shifted toward the lower energy (sp^2) value. Deconvolution of the spectra showed that the broad C 1s peaks are composed of three peaks corresponding to sp^2 carbon atoms (284.4–284.8 eV), sp^3 carbon atoms (285.3–285.7), and a third peak at about 286.2–286.6 eV that was found, which was due to some C–O contamination formed at the surface of the samples with air exposure.[14] Figure 2(a) shows that the $sp^2/(sp^2+sp^3)$ ratio increases with an increase of Ag concentration in the films. Increasing atomic percentage of silver,
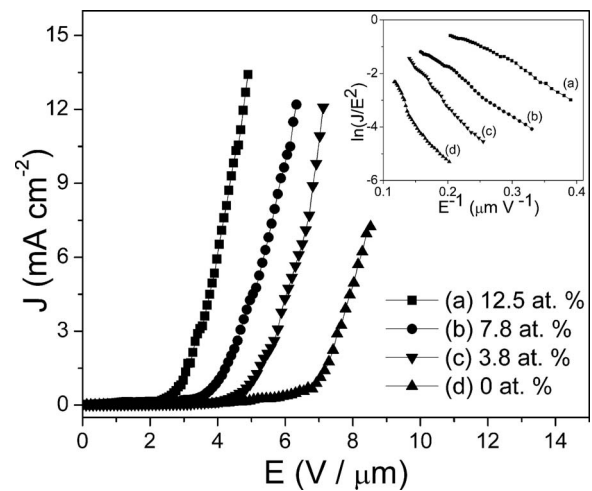
the film structure significantly changes, which is most evident from the increasing intensity of the sp^2 and the decreasing intensity of the sp^3, as well as the overall increase in the sp^2/sp^3 ratio. This means that with increasing Ag at. %, the Ag:DLC film changes to a graphitelike film.[15]

Atomic force microscopy (AFM) imaging provides more detailed information involving the surface morphology of the Ag:DLC films. Figure 2(b) shows typical AFM image of Ag:DLC film with 12.5 at. %, Ag content. The undoped DLC film generally exhibits a very smooth morphology, with the rms roughness of 1.3 nm within the surface area of 5 $\times 5$ μm^2 (not shown here). However, the rms roughness of the Ag:DLC film is approximately 3.1 nm over the area of 5×5 μm^2 [Fig. 2(b)]. The surface roughness increased with an increase of Ag concentration in the films. The presence of Ag atoms in the plasma during deposition alters the growth condition and it is observed that percentages of sp^2 bonded carbon increased with increasing Ag concentration, as discussed in XPS analysis. The surface roughness increased as the $sp^2/(sp^2+sp^3)$ ratio increases in the DLC films.[16]

From the HRTEM images, we observed that for low Ag concentration, a uniform amorphous structure was observed, i.e., the incorporated Ag atoms were dissolved in the DLC matrix. In the films of high concentration (12.5 at. %), the Ag atoms began to agglomerate and form an amorphous silver phase with a diameter of $\sim$2 nm, as shown in Fig. 2(c). The darker spots correspond to the metallic Ag region, while the brighter region corresponds to the DLC matrix. Electron diffraction pattern in the inset of Fig. 2(c) reveals that the film is amorphous even when agglomeration of Ag atoms occurs. Low deposition temperature would limit the atomic rearrangement during deposition, suppressing the crystallization of Ag clusters.

Figure 3 shows the emission current density (J) versus macroscopic field (E) curves for Ag:DLC films for different percentages of Ag at fixed anode-sample separation of 200 μm. Field emission characteristics of the films were analyzed by using the simplified Fowler–Nordheim (FN) equation given by[17]

$$\ln\left\{\frac{J}{E^2}\right\} = \ln\{ra\phi^{-1}\beta^2\} - \frac{(sb\phi^{3/2}\beta^{-1})}{E}, \qquad (1)$$

where a and b are the FN constants, ϕ is the local work function, β is the field enhancement factor, and r and s are

appropriate values of the intercept and slope correction factors, respectively. As r and s are functions varying relatively slow with $1/E$, so a FN plot is expected to be a good straight line. It has been observed that all the J-E curves (an inset of Fig. 3) in the present work are satisfactorily fitted with the FN equation, which suggests that the electrons are emitted by the cold field emission process. The threshold field (E_{th}) lies in the range of 6.8–2.6 V/μm for the variation of silver concentration in the films. It has been observed that the threshold field was greatly reduced due to silver doping. This value is quite lower than that of nitrogen doped DLC (4 V/μm),[5] sulfur doped DLC (6.97 V/μm),[8] Sn doped DLC (3.5 V/μm),[11] and aligned carbon nanofiber arrays ($\sim$3 V/μm).[18] According to the FN plot, the slope m [given by Eq. (2)] would represent the combined effect of work function and enhancement of local electric field and is given by

$$m = -\frac{b\phi^{3/2}}{\beta}, \qquad (2)$$

using $\phi = 4.7$ eV for the work function of DLC;[19,20] the field enhancement factor was calculated from the slope of the FN plot, varying in the range of 2081–5876 for different Ag at. % in Ag:DLC films. The emission mechanism may involve a strong field enhancement at the front surface. To understand the FN emission process in our Ag:DLC films, it is necessary to explain the origin of the large enhancement factor required to lower the barrier for easy electron emission. Carey *et al.*[21] and Guo *et al.*[22] proposed that the presence of sp^2 clusters within the insulating sp^3 matrix could give rise to field enhancement in a-C films containing large defect densities ($>10^{19}$ cm^{-3}). Since sp^2 clusters will have different dielectric constants, the presence of dielectric inhomogeneity is responsible for field enhancement in DLC films.[21,23] Groning *et al.*[24] explained the emission mechanism from DLC films in a way that, like a freestanding conductive tip in the vacuum, sp^2 bonded carbon clusters are assumed to form a conductive channel in an insulating matrix, which leads to local field enhancement and, hence, to an enhanced electron emission. Since the energy levels of sp^2 clusters are located at or near the Fermi level and high concentration sp^2 carbon clusters in the films play a more important role in determining the electron field emission property of the films, the effect of introducing metal into the DLC matrix allows an easier formation of sp^2 clusters.[15] From XPS analysis, it was observed that with the increase of silver concentration in the DLC films, sp^2 bonded carbon content in the films increased [shown in Fig. 2(a)]. The DLC films deposited for different percentages of Ag will consist of sp^3 matrix with varying sp^2 cluster concentration and size (from XPS and AFM analysis). TEM microstructure [Fig. 2(c)] shows that the Ag clusters are uniformly distributed in the film with the distance of at most 5 nm. Therefore, if the formation of sp^2 region is closely related to the Ag incorporation as can be deduced from Fig. 2(a), the sp^2 regions within the insulating sp^3 matrix would form conductive channels extended through the whole thickness of the film to the vacuum. The electron traversing through the channels experiences a high electric field. The effective barrier height was reduced with the addition of silver impurity in the DLC matrix. The emission current density also strongly depends on the work function. Therefore, the decrease of threshold field with the increase of

silver percentage may be due to the decrease of the effective work function of Ag:DLC films. The reason is that the high concentration sp^2 carbon clusters in the DLC films created defect induced band. From Urbach parameter calculation (not shown here), we see that with an increase of Ag at. % in the DLC films, the defect density increases. As the defect bands raise the Fermi level toward the conduction band, the work function reduced and the electron field emission property enhanced.

In summary, Ag:DLC thin film has been successfully synthesized on silicon substrates via rf reactive sputtering technique. The chemical composition, i.e., sp^2/sp^3 ratio of the DLC films, was varied by changing the Ag at. % in the films. Due to change in electronic structure by the incorporation of substitutional defect states, Ag:DLC film showed good electron field emission properties with a low-threshold field. The threshold field was estimated in the range from 2.6 to 6.8 V/μm for the films with different Ag concentrations varing from 0 to 12.5 in the films. The above study shows that the Ag:DLC films become good candidates for low-threshold field emitter among other applications.

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