



# Effect of silver doping on optical property of diamond like carbon films

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## ARTICLE INFO

Available online 4 February 2009

### Keywords:

Silver  
Diamond like carbon  
X-ray photoelectron spectroscopy  
Optical properties

## ABSTRACT

Optical properties of silver doped diamond like carbon films (Ag:DLC) deposited by the RF reactive sputtering technique were studied in detail. The chemical binding energy and the composition of the films were investigated by using an X-ray photoelectron spectroscopy. Optical transparency and optical band gap decreased with the silver incorporation to the DLC film. Optical band gap calculated from transmittance spectra decreased from 2.55 to 1.95 eV with a variation of Ag concentration from 0 to 12.5 at.%. Urbach parameter determined from the band tail of the transmittance spectra showed to increase with the doping concentration.

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## 1. Introduction

Silver incorporated diamond like carbon (Ag:DLC) has been an interesting research field of diamond like carbon (DLC) owing to its potential for solving some of the major drawbacks of pure DLC films. Ag incorporation in the DLC films reduce surface free energy and residual internal stress without sacrificing the hardness [1], increases in hydrophobic properties, improved hemocompatibility and anti-bacterial properties [2,3] and enhanced the electron field emission property with lowering the work function [4]. However, its optical properties have yet to be investigated in sufficient depth.

Optical properties of DLC films has been known to depend on the variation of chemical bonding structure and the doping such as boron, nitrogen, fluorine, phosphorous, silicon, tin, tungsten into DLC films [5–8]. The optoelectronic properties of DLC films are usually discussed in terms of transitions between occupied  $\pi$  states to unoccupied  $\pi^*$  states (associated with  $sp^2$ ) because the  $\sigma$  and  $\sigma^*$  states (associated with  $sp^3$ ) are further separated from each other. In the case of hydrogenated amorphous carbon (a-C:H) or diamond like carbon, the optical Tauc gap is given by the separation between these two bands  $2E_{\pi}$ . The larger is the average sizes of the  $sp^2$  cluster, the smaller the Tauc gap [9]. The optical band gap of the films is thus given by the average gap of the clusters in it. The distribution of  $sp^2$  gap also creates inhomogeneous disorder. The Urbach energy ( $E_u$ ), which is determined by fitting an exponential function to the slope of the absorption edge gives the disorder or defect density.

In this work we have reported the change in transparency as well as optical band gap and Urbach parameter i.e., defect density for DLC films caused by silver doping. We found that the optical properties were varied with the Ag content in the film, which showed that the advantage of the Ag:DLC would be the tunable transparency and optical band gap by changing the Ag concentration independently from other parameters.

## 2. Experimental details

The silver incorporated diamond-like carbon thin films were synthesized by the RF reactive sputtering technique at room temperature (300 K). Ultrasonically cleaned glass and silicon (400) substrates were use for deposition of Ag:DLC thin films. Silicon substrates were cleaned in 15% HF solution to clean the surface oxide layer before ultrasonically cleaning. The chamber was evacuated to a base pressure  $2 \times 10^{-6}$  mbar before deposition and then methane ( $CH_4$ ) and Argon (Ar) gases were introduced with chamber pressure at 0.1 mbar during deposition. A RF power (13.56 MHz) supply was applied in the high purity (99.99%) Ag sputter target. The details of the deposition condition for the Ag doped DLC films was described elsewhere [4].

X-ray photoelectron spectroscopy (XPS) measurements gives the binding energy of different electronic states of carbon and silver and composition i.e.,  $sp^2/sp^3$  ratio of the DLC films. XPS spectra were recorded using a Perkin-Elmer-1257 spectrometer with a hemispherical analyzer. A non-monochromatic Mg K $\alpha$  X-ray (1253.6 eV) was used as the excitation source operated at 10 kV and with an anode current 15 mA. Shirley method was applied for analysis, appropriate smoothed of the raw data and background correction. Spectrophotometric measurements were performed by using a spectrophotometer (Hitachi-U3410) at room temperature. The spectra were recorded by taking a similar glass as reference and hence transmission change due to the coating was obtained.

## 3. Results and discussion

### 3.1. Composition and bond structure

The XPS survey scan of the Ag:DLC films deposited on silicon substrate indicates clearly the contributions from C 1s (~284 eV), Ag 3d (~368 and 374 eV) and O 1s (~532 eV) peak as shown in Fig. 1(a). The core level XPS spectrum (inset of Fig. 1(a)) of Ag 3d region consists of two binding energy peaks corresponding to Ag 3d<sub>5/2</sub> (368.2 eV) and

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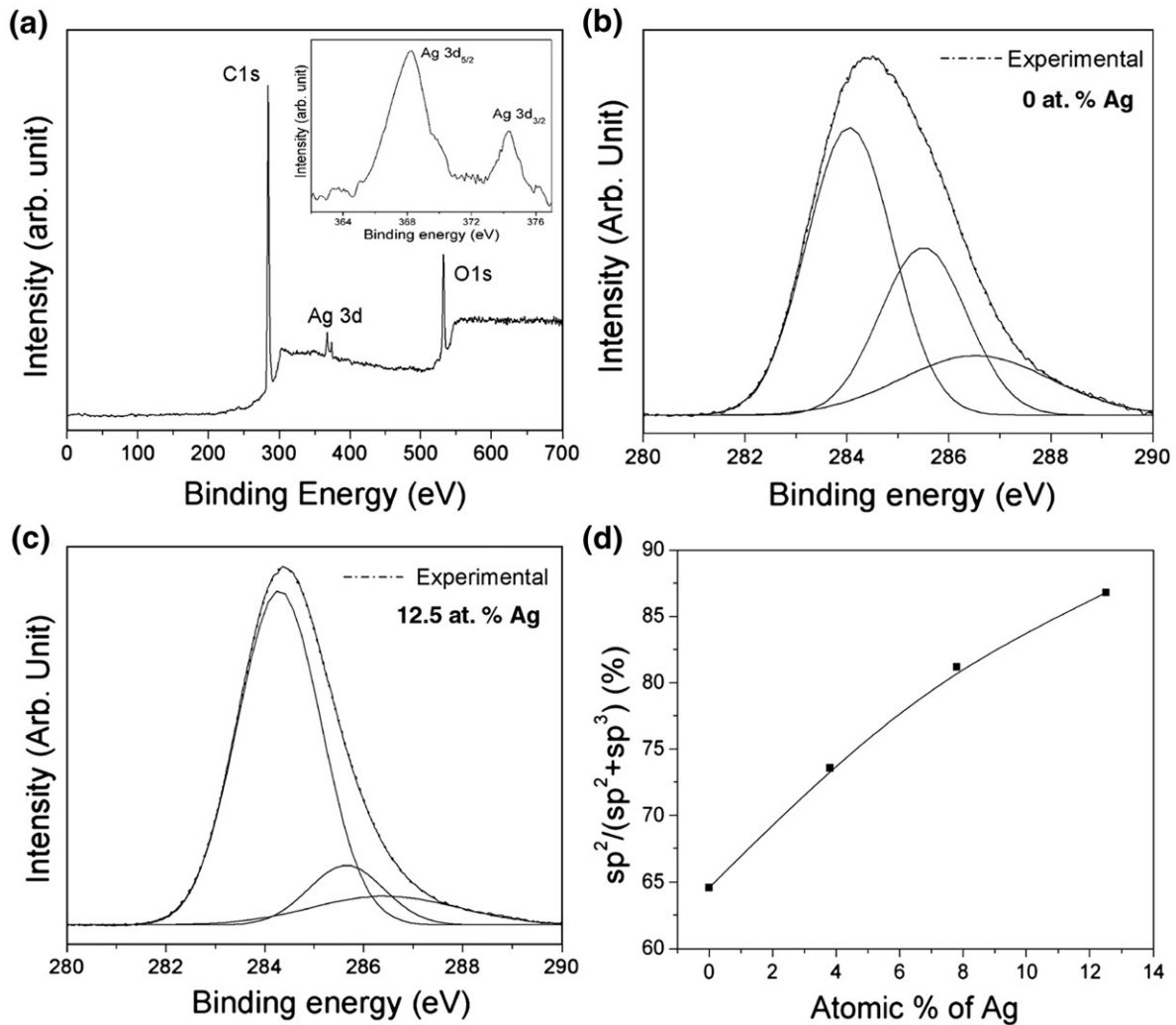


Fig. 1. (a) XPS spectra of DLC films with 12.5 at.% Ag and an inset of the Ag core level spectra, (b) and (c) deconvolution of the C 1s peak for 0% and 12.5% Ag content DLC films respectively (d) variation of  $sp^2/(sp^2+sp^3)$  ratio with at.% Ag in the DLC films.

$3d_{3/2}$  (374.2 eV) respectively, which suggests the Ag has been incorporated into the DLC matrix. The C 1s peaks obtained in this study are broad, presumably due to the differently bonded carbons to the C 1s peak. Deconvolution of the spectra showed that the broad C 1s peaks are composed of three peaks (Fig. 1 (b) and (c)) corresponding to  $sp^2$  carbon atoms (284.4–284.8 eV) and  $sp^3$  carbon atoms (285.3–285.7) respectively. Third peak at about 286.2–286.6 eV was due to some C–O contamination formed at the surface of the samples with air exposure [10]. Since XPS is a very surface sensitive technique, the detection of oxygen suggests various sources of surface contamination. Fig. 1(d) shows that the  $sp^2/(sp^2+sp^3)$  ratio increases with 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. It is thus evident that the DLC film changes to more graphitic as the Ag concentration increases.

### 3.2. Optical characterization

Fig. 2(a) shows the transmittance spectra of Ag:DLC films deposited on glass substrate. It was observed that optical transmittance reduced in the visible and near infrared region with the increase of Ag concentration in the films. Using the transmittance data and Manificier model [11], absorption coefficients were calculated in the

region of strong absorption. The optical band gap was obtained from Tauc relation as given by Eq. (1). Under the assumption of parabolic bands in an amorphous material, the relation between absorption coefficients ( $\alpha$ ) and incident photon energy ( $h\nu$ ) can be written as [12];

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g), \quad (1)$$

where  $A$  is a constant and  $E_g$  is the optical gap of the material which represents the energy difference between the valence and conduction band. Extrapolating the linear portion of the  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  plot to the  $h\nu$  axis at  $\alpha=0$ , the optical gap has been calculated from the intercept. In the inset of Fig. 2(a) showed that the optical gap of the film decreases from 2.55 to 1.95 eV for the variation of Ag percentage in DLC films.

The optical properties are likely to be controlled by the photonic effects arising from the high density of Ag particles. High resolution transmission electron microscope analysis showed that for the low concentration, incorporated Ag atoms were dispersed in the DLC matrix but for high concentration amorphous Ag atoms with diameter  $\sim 2$  nm formed and uniformly distributed with in the DLC matrix [4]. This decrease would be thus associated with the increase in the absorption by the Ag particles in carbon matrix. In addition, the decrease in the optical band gap would be also explained by the fact

that the increasing Ag concentration induces a more significant structural change to highly dominant  $sp^2$  structure (see Fig. 1). Since  $\pi$  states are more weakly bonded, they lie closer to the Fermi level than the  $\sigma$  states. Therefore filled  $\pi$  states from valence bands and empty  $\pi$  states from conduction bands determine the characteristics of gap states [13]. The optical band gap decreases with increasing the  $sp^2$  clusters as shown in Fig. 2(b). According to the cluster model of Robertson the optical band gap of DLC is dependent on the  $sp^2$  cluster size [13,14]. So, the  $sp^2$  bonds as well as the  $sp^2$  cluster size increases with silver concentration. The DLC films deposited for different at.% of Ag would consist of  $sp^3$  matrix with varying  $sp^2$  cluster concentration (from XPS analysis shown in Fig. 1(d)). As increases the Ag content in the films,  $sp^2$  content increases while optical gap decreases.

The Urbach energy is one of the standard measures of inhomogeneous disorder in amorphous carbon films [12]. Transitions between extended two localised states in amorphous semiconductors are characterised by the Urbach energy,  $E_u$ , which is determined by fitting an exponential function to the slope of the absorption edge. Urbach band tail is expressed by

$$\ln \alpha = \ln \alpha_0 - hv / E_u \quad (2)$$

where  $\alpha$  is the absorption coefficient,  $hv$  the incident photon energy,  $\alpha_0$  a constant and  $E_u$  the Urbach energy. Several factors are responsible for Urbach band tail in semiconductor such as carrier impurity

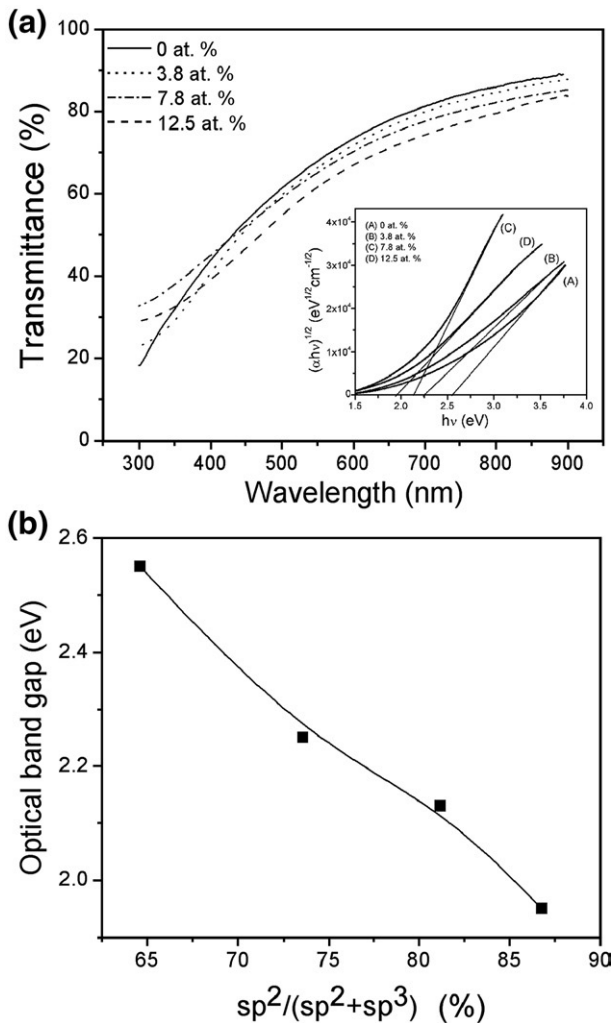


Fig. 2. (a) Transmittance spectra of the DLC films for different at.% Ag and an inset of Tauc plot to determine optical band gap and (b) variation of optical gap with  $sp^2/(sp^2+sp^3)$  ratio.

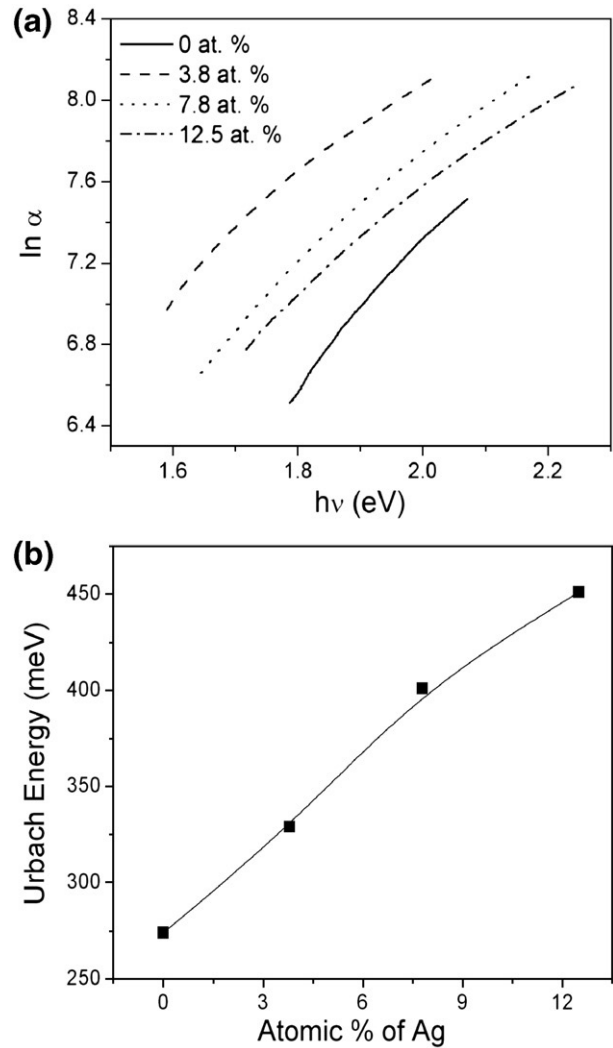


Fig. 3. (a) Plot to determine Urbach parameter and (b) variation of Urbach parameter with at.% Ag in the DLC films.

interaction, carrier–phonon interaction, structural disorder etc. Basically this parameter includes the effects of all possible defects.  $E_u$  values for different doping level were estimated from the slopes of the linear plot of  $\ln \alpha$  against  $hv$  as shown in Fig. 3 (a) and (b) indicating that increase of Ag doping in the DLC films, the Urbach parameter i.e., defect density increases.

#### 4. Conclusion

Ag:DLC thin film has been synthesized on silicon and glass substrates via RF reactive sputtering technique to characterize the optical property. 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, the transparency as well as optical band gap of Ag:DLC film changes. Optical gap decreased from 2.55 to 1.95 eV for the films with different Ag concentration varying from 0 to 12.5 at.% in the films. The potential advantage of Ag:DLC as an optical coating can be taken with controlling its transparency and optical band gap by changing the Ag content independently from other parameters.

#### Acknowledgements

The authors would like to thank Dr. K.K. Chattopadhyay, Jadavpur University, India for his helpful discussion and invaluable comments.

The present work has been supported by a grant (code #: 2E20640) from Korea Institute of Science and Technology, Republic of Korea.

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