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Appendix A. Supplementary data


REFERENCES


Thermal conductivity of nanocrystalline carbon films studied by pulsed photothermal reflectance

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ABSTRACT

The effect of nanocrystals with preferred orientation on the thermal conductivity of carbon films is studied. During graphitization, the presence of biaxial compressive stress results in the formation of preferred orientation in the microstructure of graphitic nanocrystals if the corresponding activation energy is supplied. This formation of preferred orientation leads to the orientation of graphitic basal planes perpendicular to the substrate. Due to the high thermal conductivity of graphite in the basal planes, there is a significant increase in thermal conductivity of textured nanocrystalline films compared to amorphous film.

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Graphite has among the highest (1910 W/m K) thermal conductivity in the direction parallel to basal planes while possess four orders of magnitude lower conductivity in the perpendicular direction. On the other hand, amorphous car-

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bon (a-C) has much lower thermal conductivity compared to crystalline forms of carbon. For example, tetrahedral amorphous carbon (ta-C) is shown to have conductivity of less than 1 W/m K. Increasing the percentage of sp² bonded atoms decreases the thermal conductivity significantly [1].

Anisotropic nature of graphite arises from its hexagonal structure, making it an interesting material for applications requiring directional thermal and electrical properties. Controlling the texture of the graphite basal planes in the desired direction would lead to a high degree of control on thermal conductivity. One method of achieving this is through controlling the texture during graphitization of amorphous carbon (a-C) films. Anisotropic crystal structure of graphite and intrinsic biaxial stress of a-C films lead to formation of preferred orientation of basal planes in the direction perpendicular to the substrate when external force field and respective activation energy is supplied to the system [2,3]. McKenzie et al. show that upon graphitization, the Gibbs free energy of the system and hence the orientation of the graphitic nanocrystals strongly depends on the stress state of the film. It is shown that since the stress field in a-C film is a compressive biaxial stress in the growth plane, the system will have its lowest possible Gibbs free energy when the basal planes are oriented perpendicular to the substrate. It has been shown that this preferred orientation results in outstanding changes in electrical properties of carbon films [4,5]. However, there is no reported work on thermal conductivity of such films. As such, the thermal conductivity of textured carbon films will be addressed in this letter.

Fig. 1 – Typical TEM image of carbon films deposited at 200 V substrate bias and (A) room temperature and 200 °C and (B) 300 °C and 400 °C.

Fig. 2 – (A) Low loss and (B) high loss EEL spectra of carbon films deposited at 200 V substrate bias and different temperatures.
Ninety nanometers thick carbon films were prepared using the double bend filtered cathodic vacuum arc (FCVA) [6]. The microstructure of the films was investigated by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). Pulsed photothermal reflectance (PPR) [7] technique was used to investigate the thermal conductivity of the films.

Fig. 1 shows the HRTEM image of the carbon films deposited at 200 V substrate bias and different temperatures. The films deposited at room temperature and 200 °C is purely amorphous and no preferred orientation can be observed in the microstructure. On the other hand, the samples deposited at 300 °C and 400 °C show a much different microstructure with their basal planes oriented in the perpendicular direction with respect to the substrate. The presence of discontinuous arcs in the diffraction pattern which can be indexed as the diffraction of (002) planes confirms the formation of preferred orientation in the microstructure of the film.

Fig. 2 shows the low-loss and high-loss EEL spectra of the films. The low-loss EEL spectra of the room temperature and 200 °C deposited film show a single bulk plasmon excitation in the range of 25–30 eV. Low-loss EEL spectra of 300 °C and 400 °C deposited films reveal a π plasmon shoulder at about 5 eV which further confirms the presence of ordering in π bonds. Carbon K-edge EEL spectra of the films shows a
\( \pi \rightarrow \pi^* \) transition at 285 eV and a broad \( \sigma \rightarrow \pi^* \) band. Considering the shape of \( \sigma \rightarrow \pi^* \) band, it can be concluded that the room temperature and 200 °C deposited carbon films are amorphous in structure while the presence of a peak at 293 eV in the EEL spectrum of 300 V and 400 V deposited carbon films confirms the presence of crystalline graphitic carbon in the structure [8].

Thermal conductivity of a-C films have been investigated by different groups and it was found that increase in density and hence the sp\(^3\) content increases the conductivity of the films. Therefore depending on the density of the film, thermal conductivity of 0.2–3.5 W/m K can be achieved [1]. It was also found that the presence of small sp\(^3\) nanoclusters in sp\(^2\) rich carbon films increases the conductivity significantly [9].

Fig. 3 shows the PPR spectra of the carbon film deposited at different temperatures and conductivities are shown in Fig. 4. Three layer model (Eq. (1)) has been used to fit the experimental data [10]:

\[
T(5) = \frac{Q_0}{\epsilon_i \rho c_i S} \left( \cos \theta_i \cos \theta_j \varepsilon_i \varepsilon_j \right) \left( \cos \theta_i \cos \theta_j \varepsilon_i \varepsilon_j \right) \left( \cos \theta_i \cos \theta_j \varepsilon_i \varepsilon_j \right) \left( \cos \theta_i \sin \theta_j \varepsilon_i \sin \theta_j \varepsilon_j \right) \left( \cos \theta_i \sin \theta_j \varepsilon_i \sin \theta_j \varepsilon_j \right)
\]

where \( \epsilon_i = \sqrt{\mu_i C_i}, \epsilon_i = \epsilon_i / \epsilon_i, \eta_i = d_i / \eta_i \) and \( i = 1,2,3 \). Subscripts 1, 2 and 3 are labels for gold, carbon and silicon, respectively. \( S, \rho, C, K, \epsilon, \eta, \) and \( d \) are the frequency, bulk density, specific heat, thermal conductivity, thermal effusivity, thermal diffusivity, and thickness of each layer, respectively. Q(0) is the Laplace transform of the Nd:YAG laser pulse. Eq. (1) is then inversely Laplace transformed into time domain using Stehfest numerical method and is used to fit the experimental data. The pump and probe spot sizes were 3 mm and 1 mm, respectively. It should also be noted that since the pump spot size is much larger than the lateral heat diffusion length (~11 \( \mu \)m) the heat transfer can be assumed as one dimensional. Therefore, regardless of the nature of the materials under study, PPR can be used to measure the thermal conductivity of thin films in the direction perpendicular to the pump laser.

The room temperature deposited film possesses a very low conductivity of 0.95 W/m K. The low-loss EEL spectrum of this sample shows a bulk plasmon peak at 28.2 eV which corresponds to density of 2.5 g/cm\(^3\). The low conductivity is expected considering the pure amorphous structure as well as the low sp\(^3\) content of the film. As confirmed by Raman spectroscopy (not shown here), increasing the deposition temperature to 200 °C, leads to formation of conductive sp\(^2\) nanoclusters in the structure which increases the conductivity to 3.2 W/m K which is in agreement with the previous work of Kelly [9]. It should be noted that previous works on pure a-C [1] showed that decreasing the density leads to decreases in the conductivity. However, as it is shown here, the presence of sp\(^2\) clusters increases the conductivity significantly.

Further increases in deposition temperatures increase the thermal conductivity. The 300 °C and 400 °C deposited films possess thermal conductivities of 5.32 W/m K and 16.72 W/m K, respectively. Increase in conductivity can be interpreted through the formation of preferred orientation in the microstructure of the film. Formation of texture in the a-C matrix, results in formation of graphitic planes perpendicular to the substrate. Hence, the thermal conductivity of high temperature deposited films is increased significantly. The increase in the conductivity of 400 °C deposited film compared to that of 300 °C deposited can be understood by considering the high-loss EEL spectra of these two films. The \( \pi \rightarrow \pi^* / \sigma \rightarrow \pi^* \) ratio for the film deposited at 300 °C is 0.58 while the same ratio for 400 °C deposited film is 0.66. Increase in \( \pi \rightarrow \pi^* / \sigma \rightarrow \pi^* \) ratio shows that (002) planes are more ordered in the direction parallel to the electron beam (perpendicular to the substrate). Therefore, preferred orientation is enhanced in 400 °C deposited film compared to that deposited at 300 °C and therefore the thermal conductivity is increased.

In conclusion, the effect of preferred orientation on the thermal conductivity of carbon films is studied. It is shown that even formation of nanocrystalline sp\(^2\) bonded clusters increases the conductivity. However, formation of preferred orientation significantly increases the thermal conductivity in the perpendicular direction to the substrate which is due to reorientation of graphitic basal planes with very high conductivity.

\textbf{REFERENCES}