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Effect of temperature on sulfur-doped diamond-like carbon films deposited by pulsed laser ablation[☆☆]

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ABSTRACT

In this study, S-DLC films were deposited using pulsed laser ablation of a novel sulfur–graphite (SG) mixture target using an ArF excimer laser (193 nm). The SG targets were made by mixing sulfur and graphite powders at different sulfur molar percentages from 0% to 25%. The S-DLC films were deposited at room temperature, 150 °C and 250 °C. The optical and electronic properties of the doped films were studied. Laser Raman spectroscopy indicated increased graphitic behavior with temperature but decreased with higher sulfur content. Spectroscopic ellipsometry analyses found that the optical band-gap energy, extinction coefficient and reflective index, clearly depended on deposition temperature and sulfur content. Hall Effect measurements indicated n-type carrier with concentration in the range of 1×10^{14} to 2×10^{17} cm^{-3}, strongly depended upon the deposition temperature and amount of sulfur.

1. Introduction

Diamond-like carbon (DLC) films have been intensively studied and widely used in many applications due to their useful properties, which are similar to those of diamond. These include high hardness, wear corrosion protection, good thermal stability, chemical inertness as well as high optical transparency [1,2]. These properties allow DLC films to be used in many applications, such as anti-reflective coatings on optics, cutting and abrasive wear tools, IR windows, computer hard disk coatings, bio-resistant coatings for medical implants, watch cases and lenses, etc. [3–5]. DLC films have been developed for electronic application by doping them with impurity atoms in order to increase the carrier concentration and control the conductivity. The doping of DLC films both with p-type and n-type dopants has been reported [6–9]. DLC films with p-type doping can be achieved using boron and iodine as dopants. Attempts to fabricate DLC films with n-type doping with phosphorus and nitrogen were reported in only few papers, however, most works yield unsatisfactory results. Recent research has been focused on the possibility of n-type doping of DLC with sulfur. It is foreseeable that the band-gap of sulfur-doped diamond-like carbon (S-DLC) films can be tuned to be between 0 and 4 eV depending on the deposition techniques and doping conditions. In this regard, the utilization of sulfur as an alternative dopant for n-type doping of DLC films is of high interest.

There are several deposition techniques that can be used to produce DLC films, such as plasma-enhanced chemical vapor deposition (PECVD) [10,11], sputtering [12,13] as well as pulsed laser ablation (PLA) [9,14–19]. In general, PLA is a favorable technique since it can fabricate DLC films with high quality and high proportion of sp^3 hybridization. However, one of the main advantages of PLA which is the capability to yield hydrogen-free material might not be very helpful for the doping of DLC. A general question in doping of amorphous semiconductors is if the defect density is low enough. Defects reduce the diffusion length of carriers. They also inhibit any doping, because dopants must donate enough carriers to sweep the Fermi level through these defect states. DLC possesses a high paramagnetic defect density of the order of 10^{18} to 10^{20} cm^{-3} [20,21]. This is the case even in the hydrogenated forms. In amorphous silicon, the addition of hydrogen can result in several orders of magnitude decrease in the defect density [22] which allows the possibility of amorphous silicon doping. Unlike in amorphous silicon, hydrogen does not seem to efficiently passivate defects in amorphous carbon. It is reported that the presence of the large hydrogen content of up to 55% in hydrogenated amorphous carbon does not reduce defect densities by passivating unpaired electrons [23], which is contrast to the case of hydrogenated amorphous silicon.

In present work, we report the growth of DLC films with sulfur as dopant in order to create an n-type semiconductor. To the best of our knowledge, fabrication and characterization of sulfur doped DLC (S-DLC) film deposited by PLA technique has not been previously reported.

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2. Experimental setup

DLC and S-DLC films were deposited on 10 × 10 mm silicon substrates by PLA using a target made from pure graphite or a mixture of sulfur and graphite, respectively. The sulfur–graphite (SG) mixture targets were made by mixing sulfur and graphite powders (nominal purities > 99.999%) at different sulfur molar percentages from 0% to 25% and pressing them at 10 tons pressure in a hydraulic press. The process yield firm solid targets with smooth surfaces which could be placed into the vacuum system. The PLA laser source was an ArF excimer laser beam with wavelength of 193 nm and 20 ns FWHM. The laser fluence was set at 10 J/cm^2 with 10 Hz repetition rate. The laser beam was introduced into the vacuum chamber through an anti-reflection-coated convex focusing lens and then the chamber quartz window. The laser beam was focused on the rotating target. The laser spot size on the SG target surface was 1.0 × 0.4 mm^2. The deposition chamber was evacuated by a rotary and a turbomolecular pump yielding a typical base pressure of 1×10^{-6} Torr. The Si substrate was placed approximately 4 cm from the target such that ablated material from the target could strike the front surface of the substrate and stick to it. A continuous wave (CW) CO_2 laser focused onto the backside of a substrate was employed to heat the substrate controllably by adjustment of the CO_2 laser output power. DLC and S-DLC films were deposited at various temperatures, including room temperature, 150 °C and 250 °C.

The effects of the deposition temperature upon the structural and optical properties of the S-DLC films were studied. All DLC and S-DLC deposited films were analyzed for diamond-like carbon formation by using Laser Raman Spectroscopy (Renishaw-2000), equipped with an argon ion laser excitation at $\lambda = 514$ nm and a power of 20 mW with a 50× objective. A Woollam VASE Ellipsometer at an incidence angle of 50°, 55°, 60°, 65° and 70° in the 1.0–5.0 eV range of photon energy was used to analyze the optical properties of films. The AC Hall Effect measurements in a magnetic field of 0.6 T at room temperature were used to identify the carrier concentration of S-DLC films. The morphology of films was analyzed by scanning electron microscopy (SEM).

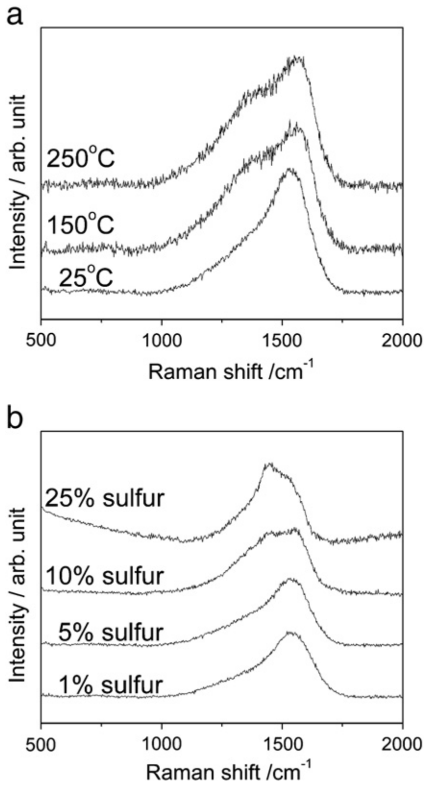

Fig. 1. Raman spectra of S-DLC films deposited at 10 J/cm^2 of laser fluence on silicon substrate at (a) 5% sulfur molar content in the SG target and different temperatures (b) different sulfur molar percentages and room temperature.

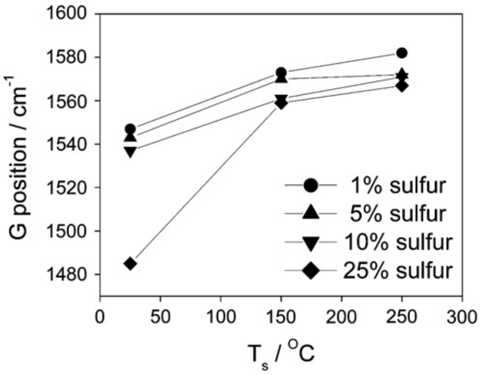

Fig. 2. A plot of G-peak position of S-DLC films versus substrate deposition temperatures (T_s) at different target sulfur molar percentages.

3. Results and discussions

All of the Raman spectra were deconvoluted into two Gaussian peaks, the D (disordered) and G (ordered graphite) peaks, centered at approximately 1360 cm^{-1} and 1560 cm^{-1}, respectively. In the fitting of these spectra, the G-peak position was found to be a significant parameter and a sensitive measure of the structural change of sp^2 hybridized carbon domains. As such, it helps to determine the amount of graphite cluster size in the films. Raman spectra of S-DLC films deposited at different temperatures and from 5% sulfur molar in the SG target are shown in Fig. 1(a), and at different sulfur molar percentages from 0% to 25% and room temperature in Fig. 1(b). As the structure of S-DLC films changes, the G peak position is upshifted with decreasing sp^3 fraction. The G-peak position of S-DLC films deposited at different substrate temperature and sulfur molar percentage is shown in Fig. 2. It was found that at the same percentage of sulfur doped in S-DLC films, the graphite peak shifted upward to higher frequency with increasing substrate temperature. This upward shift behavior in the G-peak is probably due to an increase in the number of graphite clusters in the S-DLC films. Therefore, the Raman spectra indicate increased graphitic behavior, with larger numbers of graphite clusters at the higher substrate temperature. For a constant substrate temperature, the graphite peak shifted to lower frequency with increasing sulfur content in the S-DLC films. This indicated decreased graphite behavior with smaller numbers of graphite clusters at the higher sulfur content. Moreover, the graphite behavior in S-DLC films can be used to predict the optical band gap, which is proportional to amount of graphite in S-DLC films (see later).

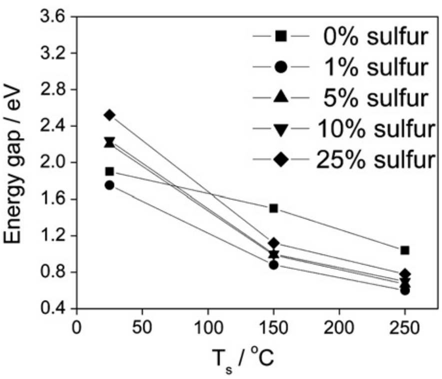

Fig. 3. A plot of Tauc energy gap of S-DLC films versus substrate deposition temperatures (T_s) at different target sulfur molar percentages.

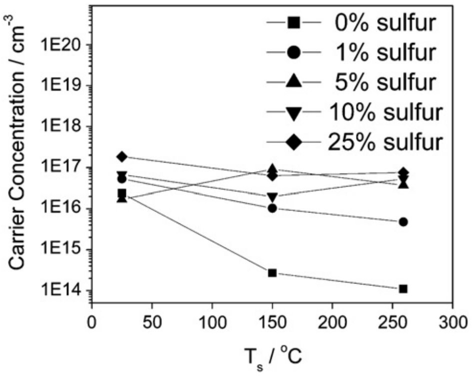

Fig. 4. A plot of carrier concentration of S-DLC films versus substrate deposition temperatures (T_s) at different target sulfur molar percentages.

Spectroscopic ellipsometry was used to determine the optical band gap energy (E_g) of the S-DLC films. When the refractive index (n) and extinction coefficient (k) value are obtained, E_g can be determined by following the relation $\varepsilon_i(E)=B(E-E_g)^2/E^2$, where $\varepsilon_i=2nk$ and B is a constant. A plot of the photon energy (E) with the quantity $E\varepsilon_i^{1/2}$ allows E_g to be determined by extrapolation. The values for E_g of S-DLC films deposited at different substrate temperatures and sulfur molar percentages are shown in Fig. 3. E_g of S-DLC films at room temperature was found to be in the range of 1.7–2.6 eV, and decreased gradually to be in the range of 0.4–1.2 eV at 150 °C and 250 °C. At the same substrate temperature, E_g of S-DLC films was found to increase with increasing sulfur molar percentage. This means that sulfur affects a structural change on the S-DLC films. The graphite behavior should be decreased with higher sulfur molar percentage. In the case of S-DLC films at the same sulfur molar percentage, the substrate temperature still has an effect on the optical band gap of films: E_g decreases at higher substrate temperature. Films have more graphite behavior at higher substrate temperature. These results also assist in promoting the structure change of S-DLC films.

The carrier concentration of the S-DLC films is another parameter which is of interest for electronic applications. The carrier concentration of S-DLC films was investigated by Hall Effect measurements at room temperature. It is has been reported in both experimental and simulation works [24,25] that inhomogeneities present in the sample could lead to incorrect conclusions about carrier type in Hall Effect measurements. According to Bierwagen et al. [25], measured carrier types are not affected by inhomogeneities in carrier mobility if the carrier concentration can be kept homogeneous. In contrary, incorrect assignment of the carrier type can be a consequence of lateral inhomogeneities in carrier concentrations. Apparently, when carrying out Hall Effect experiments, careful attentions must paid on the placement of contacts. If the contacts are at the sample corners as opposed to at the interior of the sample, incorrect results can be avoided. Qualitatively correct carrier concentration values close to the average carrier concentration in the sample can be obtained upon correct placement of contacts in the measurements.

Since the homogeneity of the samples has not been measured, careful placements of contacts in Hall experiment were carried out at the edges of the samples in our experiments in order to avoid wrong conclusions about carrier type. The result of Hall Effect measurements is shown in Fig. 4. It was found that the carrier concentration was in the range of 1×10^{14} to 2×10^{17} cm^{-3}. The effect of doping the DLC films with sulfur was found to convert the films into an n-type semiconductor. The carrier concentration of S-DLC films increased with increasing of sulfur molar percentage for constant substrate temperature. A possible reason is that when the sulfur molar percentage in the target increases, the probability of incorporation of sulfur into DLC films would also increases. Hence, the carrier concentration of S-DLC films increases. Films deposited at room temperature were found to have higher carrier concentration than the films at 150 °C and 250 °C. Due to the melting point of sulfur ~112.8 °C, sulfur may be preferentially evaporated out of the target

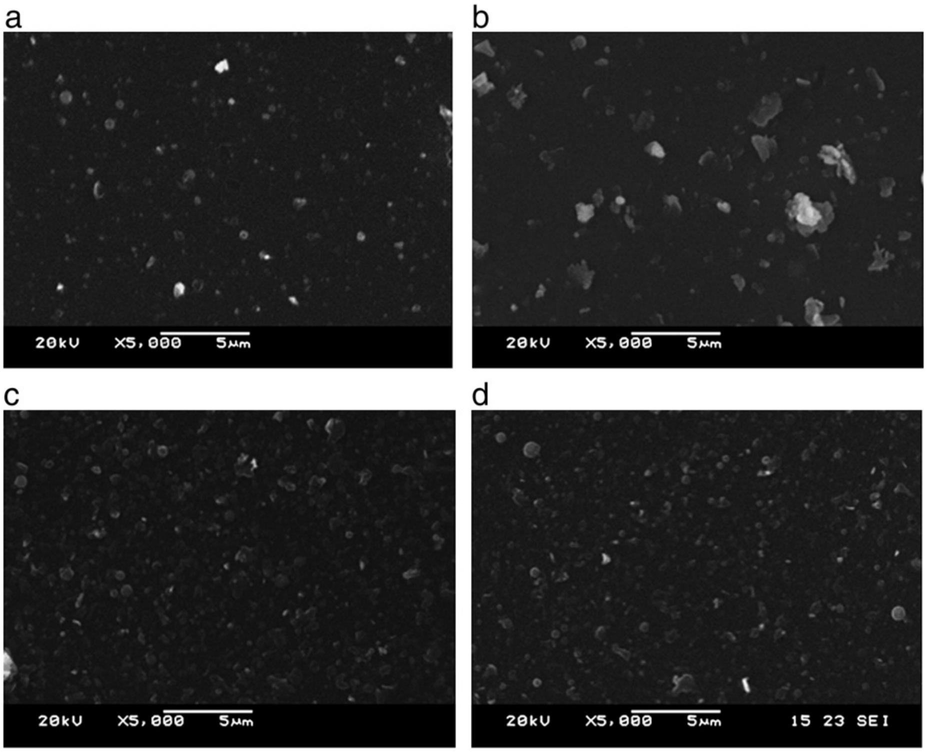

Fig. 5. SEM images of S-DLC films deposited from targets with different molar percentages of S: (a) 10% and room temperature (b) 25% and room temperature (c) 10% and 150 °C (d) 10% and 250 °C.

before the ablation process occurs. Therefore, the amount of sulfur that is incorporated into the substrate decreases with increasing substrate temperature for the same sulfur molar percentage in the target. These changes in sulfur content in the films then affect the carrier concentration of S-DLC films.

The morphology of the S-DLC films was investigated by scanning electron microscopy (SEM). The morphology of S-DLC films deposited at room temperature with 10% and 25% sulfur molar are shown in Fig. 5(a) and (b), respectively. Fig. 5(c) and (d) shows the morphology of S-DLC films with 10% of sulfur molar at 150 °C and 250 °C, respectively. Micron-sized particulates were found on the surface of S-DLC films. The number of larger particulates increased with increasing amount of sulfur in the target. S-DLC films at 150 °C were rougher than the films at room temperature. This is because a large number of small particulates were deposited on the surface of the films at this temperature. For S-DLC films at 250 °C, the surface appears compressed and smooth with many particulates. Therefore, the surface of films at 250 °C looks smoother than the films at 150 °C. In a certain regard, this particulate problem is intrinsic to the PLA process, and holds back its use in many electronic and optical applications which require extreme surface smoothness. In this work, the targets were formed from compressed graphite and sulfur powder admixture, which could contain cracks, protrusions and trapped gasses. These would be the main causes of particulates in this work.

4. Conclusions

In conclusion, this is the first report of sulfur doped DLC films by PLA technique which shows the effect of sulfur doping on DLC films with different substrate temperatures, E_g and in which the structure of S-DLC films was found to be altered. The results indicate that sulfur doped DLC films can act as n-type semiconductors with carrier concentrations in the range of 1×10^{14} to 2×10^{17} cm^{-3}. The optical band gap was found to be in the range of 0.4–2.6 eV. The Raman results showed increased graphitic behavior at high deposition temperature and low sulfur molar percentage. These results are consistent with the optical band gap measured by SE and the carrier concentrations measured by Hall Effect. The smoothness of the S-DLC films depends upon the substrate temperature and amount of sulfur in the target.

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