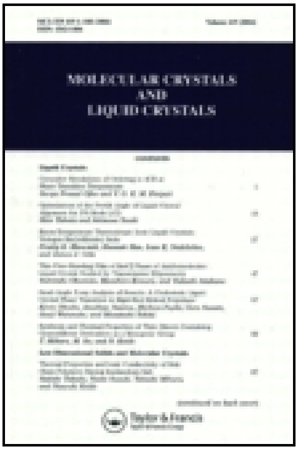

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INVESTIGATION ON ANTI-REFLECTION PROPERTY OF NITROGEN DOPED DIAMOND-LIKE CARBON (DLC) FILMS PRODUCED BY RF MAGNETRON SPUTTERING

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Nitrogen doped Diamond-like carbon thin films were deposited on n-Si and SiO_2 substrates by rf magnetron sputtering using pure graphite (99.999%) as the target material and mixtures of Ar, N_2 and H_2 for plasma generation. The dependence of structural and optical properties on nitrogen content was investigated using XPS, Raman spectroscopy, FT-IR spectroscopy, and Ellipsometry studies. It was found that as the nitrogen content was increased in the plasma, sp^2 bonding favored. Also it was observed that oxygen contamination increased with nitrogen content. Typical C-H stretching modes connected with diamond-like carbon could be seen in FT-IR spectra. The D and G bands were well defined and it was observed that as nitrogen content increased G band was enhanced. Ellipsometry studies revealed that the optical constants like refractive index (n) and extinction co-efficient (k) increased with increase in nitrogen content as well as substrate temperature.

Keywords: diamond-like carbon; anti-reflection; ellipsometry; refractive index; extinction co-efficient

1. INTRODUCTION

DLC is an amorphous material mainly comprising of sp^2 and sp^3 bonded carbon atoms. Due to its unique properties such as hardness, chemical inertness, good mechanical adhesion, high dielectric strength, tunable refractive index, etc. it has applications in various fields [1]. These DLC films can be prepared by a lot of techniques. However all these techniques use hydrocarbons for generating plasma. Here we employ rf magnetron sputtering and the plasma gas is a mixture of argon, nitrogen and hydrogen. These films have a complicated network of carbon atoms of different hybridized states [2] with hydrogen included in atomic and molecular form. The main aim of this study is to determine the possibility of application of DLC coating (doped with nitrogen) as a good anti-reflection coating for solar cells, thereby increasing the efficiency of these cells.

2. EXPERIMENTAL

Here in our study rf magnetron sputtering technique was employed to produce DLC films. The rf (13.56 MHz) power was 100 w. Pure graphite (99.999%) was used as target and the deposition was carried out on n-Si and SiO_2 substrates ($8 \times 8\,mm^2$, 0.5 mm thick). The plasma gas comprised of different concentrations of nitrogen and hydrogen along with argon. The target was at a distance of 4 cm from the substrate. The total working gas pressure was 1 Pa and deposition time was 0.5, 1 and 2 hour. Deposition was carried out for different substrate temperature (50, 100, 150, and 200°C) under same plasma conditions to understand the effect of substrate temperature on properties of these films. The deposited films were then subjected to various surface studies to understand bonding nature of these of films. Optical studies were also carried out to exploit the optical properties of these films. XPS studies were done to estimate the concentration of relative elements present in the films. Raman and FT-IR spectroscopic studies were done to understand the chemical nature of these films. The primary optical constants such as refractive index (n) and extinction coefficient (k) were determined using laser ellipsometry.

3. RESULTS AND DISCUSSION

The deposited films were subjected to these characterization techniques to understand the properties of these films.

3.1. XPS Analysis

Typical C1s and N1s spectra were seen by XPS studies. To check the bonding states of C in the a-C:H:N films, the C1s peak was de-convoluted with 4 Gaussian bands [3,4]. On comparing the de-convoluted peaks for different samples the following features were observed: sp^2CN bonding was favored as nitrogen content in the plasma increased. The oxygen contamination was found to increase as nitrogen content in the plasma increased. It was observed that carbon was present in graphitic form as well as diamond-like form. In a similar manner, the N1s peak was de-convoluted using three Gaussian bands.

The N/C ratio of the films deposited at different nitrogen plasma conditions were obtained from the integral areas of C1s and N1s peak using the photo-ionization cross-section of each element [5]. The N/C ratio increased with increase in nitrogen content in the plasma. N/C ratios were 0.14, 0.3, and 0.36 for the plasmas containing 10%, 30%, and 50% nitrogen respectively.

3.2. Raman Spectroscopy

Raman spectroscopic studies were done to get an idea about the D and G bands for these films. For hard carbon films, the spectra of amorphous and diamond-like carbon can be band-fit to separate the contributions of the "graphitic carbon" (G band) from the "disordered band" (D band). Typical Raman spectra for our film is shown in Figure 1. It was observed that as nitrogen content increases the G band was enhanced. This implied that the structure was being more and more graphitic implying that more sp^2 bonding was favored. In case of pure a-C:H films the ratio of the intensity of the D band to G band (I_D/I_G) ratio was less than one. It was observed that the I_D/I_G ratio increased with increase in the substrate temperature.

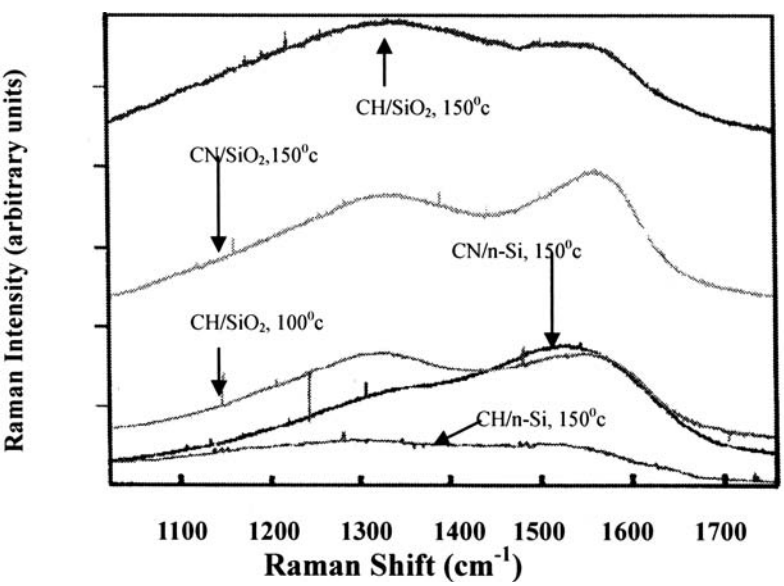

FIGURE 1 Raman spectra of a-C:H:N films of various compositions.

3.3. FT-IR Spectroscopy

The infra-red absorption spectra are shown in Figure 2. It consists of a broad band at 1000–1600 cm^{-1}; C≡N stretching at 2100–2250 cm^{-1}; C-H stretching mode at 2800–3000 cm^{-1}; N-H stretching mode at 2800–3000 cm^{-1}. The broad band at 1000–1600 cm^{-1} is attributed to carbon matrix of nitrogen atoms. This band can be deconvoluted to 2 bands which are quite similar to D and G bands found in Raman spectroscopy [6]. The one located near 1400–1600 cm^{-1} is due to the presence of large sp^2 domains while the other near 1250–1400 cm^{-1} is due to sp^3 domains [7].

A peak shift is observed as nitrogen content in the plasma increases. The band at 1400–1600 cm^{-1} is found to increase as nitrogen content increases and this implies that sp^2 CN bonding is favored and this corresponds to the results stated earlier. C≡N stretching modes were found at 2100–2250 cm^{-1} and N-H stretching modes were found at 3200–3500 cm^{-1} according to assignment in molecules [8]. The peak height of CN bonding was found to be enhanced as nitrogen content increases. The absorption band at 2800–3000 cm^{-1} is identified with C-H stretching vibration, which is attributed to diamond-like carbon film [9,10]. As nitrogen content increased this peak was found to be de enhanced showing that the bonding was more likely to graphitic than diamond-like structure.

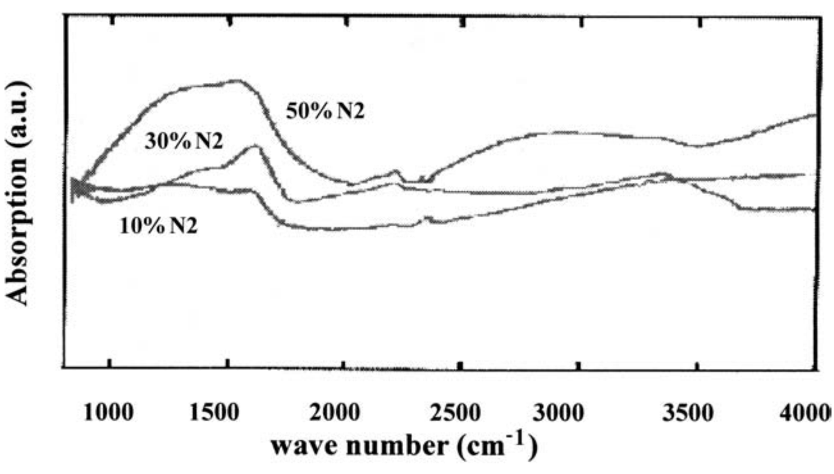

FIGURE 2 FT-IR absorption spectra of a-C:H:N films deposited at 3 different nitrogen contents in the plasma.

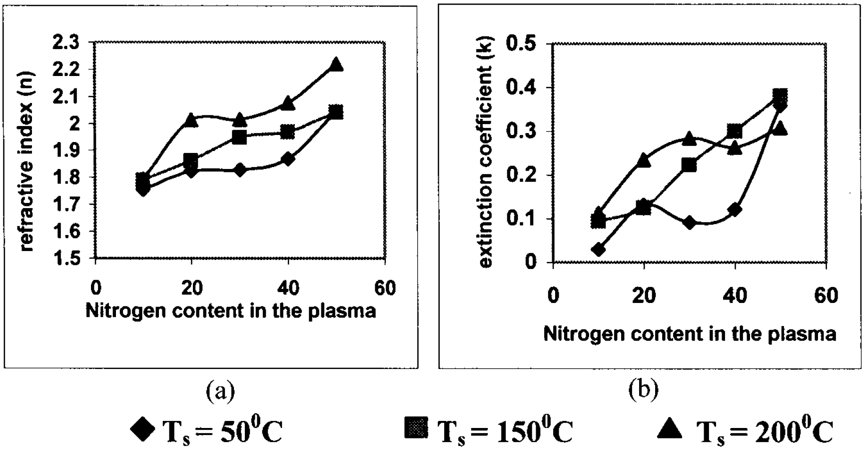

FIGURE 3 (**a**) Variation of refractive index (n) as a function of nitrogen content; (**b**) Variation of extinction coefficient (k) as a function of nitrogen content.

3.4. Ellipsometry

In order to understand the optical properties of these films the samples were subjected to ellipsometry measurements. An He-Ne laser was used at a fixed angle of incidence of 70° to determine the main optical constants like refractive index (n) and extinction coefficient (k). Figures 3a and 3b shows the variation of refractive index and extinction coefficient as a function of nitrogen content. It was observed that as nitrogen content increased the values of n and k increased and a similar trend was observed with increase in substrate temperature.

In order for a film to exhibit good anti-reflection property, it should have minimum reflectance and this is attained if the following condition is satisfied. The refractive index (n_f) of the film should be equal to the square root of the refractive index (n_s) of the substrate [11]. Here we found that 30% N_2 content sample has $n = 1.97$ which is the required one for a Si substrate whose refractive index is 3.88. It was observed from ellipsometry that 30% nitrogen content sample had some good anti-reflection property.

4. CONCLUSION

Nitrogenated Diamond-like carbon (DLC) thin films were deposited on n-Si and SiO_2 substrates at different conditions. From XPS studies it is observed that the carbon is present in both graphitic and diamond-like structure. It is observed that nitrogen content greatly favored sp^2 bonding. Increase in nitrogen content led to oxygen contamination. Raman and FT-IR spectroscopic studies proved the existence of hydrogen and nitrogen inside the film. Various typical stretching modes were observed. Typical D and G bands were also found. I_D/I_G ratio increased as substrate temperature increased. Typical C-H stretching attributed to DLC structure was found and this proves that the carbon is present in DLC form also. Ellipsometry studies revealed that the optical constants such as refractive index and extinction co-efficient could be altered by suitably changing the nitrogen content and substrate temperature. Both n and k were found to increase with increase in nitrogen content and substrate temperature.

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