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LETTER TO THE EDITOR

The effect of sputtering ions on the structure and properties of diamond-like carbon films

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Abstract. Carbon films have been deposited on Al₂O₃(0001) substrates by sputtering a graphite target with 3 keV CH₄⁺, N⁺, and Ar⁺ ions. The structure and properties of the films were examined by Auger electron spectrometry, micro-Raman spectroscopy, and optical absorption measurement, and were found to be dependent on which sputtering ions were used. The stability of the carbon films was also examined using Fourier-transformed infra-red spectroscopy by annealing the films at temperatures from 25 to 200 °C.

Diamond-like carbon (DLC) films have attracted much research interest in recent years due to the potential applications of their novel properties [1–4]. Various techniques, e.g., ion beam and ion sputtering deposition [5, 6], pulsed laser ablation of graphite [7], plasma-enhanced chemical vapour deposition (CVD), and ion-assisted deposition [8], have been developed and used to form DLC films. From previous studies it is known that in DLC films both sp² and sp³ hybridizations are present, and that the diamond-like properties of the films are largely determined by the sp³/sp² ratio. A promising way to improve the film properties is thus to increase the sp³/sp² ratio during the film growth. It has been reported recently that, by means of a special type of direct ion beam deposition, i.e. mass-selected ion beam deposition, carbon films with an sp³ fraction as high as 80%—namely tetrahedral amorphous carbon (ta-C) films—are obtainable [9]. For ion beam sputtering deposition, however, until now only DLC films with low sp³ fractions have been achieved. It is therefore of interest to investigate the possibility of producing carbon films with good properties and to make clear the mechanism of the carbon film growth that occurs in this approach.

In the present study, we employ the ion beam sputtering deposition process to form diamond-like carbon films, and to investigate the influence of which sputtering ions are used on the structure and properties of the films.

Diamond-like carbon films were deposited on Al₂O₃(0001) substrates at room temperature by sputtering a graphite target in an ultrahigh-vacuum chamber with different ions, i.e. 3 keV N⁺, CH₄⁺, and Ar⁺. The chamber was maintained by an ion pump, a titanium sublimation pump, and a turbo-molecular pump, and had a vacuum level of the order of 10^{−9} Torr. The graphite target was sputtered by the energetic ions with an angle of incidence of 45° with a beam current density of about 10 μA cm^{−2}. After the deposition, the structure of the films was checked in the chamber by Auger electron spectrometry (AES) with 3 keV electrons, and later by micro-Raman spectroscopy excited with a 514 nm Ar⁺ laser. The optical properties of

the carbon films were examined by measuring the absorption using optical spectroscopy in the visible and ultra-violet range. The thermal stability of the films was examined using Fourier-transformed infra-red (FTIR) spectroscopy by annealing the films at elevated temperatures in air.

Figure 1 shows the carbon AES KLL spectra of the films prepared on $\text{Al}_2\text{O}_3(0001)$ by sputtering the graphite target with 3 keV Ar^+ and N^+ ions. The film prepared by CH_4^+ sputtering has an AES spectrum similar to that of the N^+ -sputtered one. The Ar^+ -sputtered film has typical AES line shapes of DLC films, i.e. a big dip at around 273 eV, a large peak at 250 eV (designated as G), and a small peak at about 260 eV (designated as D). The N^+ -sputtered film, however, has different KLL line shapes. One sees from the figure that the intensity of the D peak of the N^+ -sputtered film is considerably increased, and is comparable to that of the G peak. Since the position of the D peak with respect to that of the G peak is the feature in which diamond distinctly differs from graphite, the increase in the intensity of the D peak implies an increase in the sp^3 content [10–15]. Using the minimum between the D and G peaks as the reference, a peak intensity ratio of D/G can be obtained directly from the spectrum, which is a reasonable measure of the sp^3 fraction in the film [16]. The D/G intensity ratio is calculated to be about 0.0 and 0.6 for the Ar^+ - and N^+ -sputtered films respectively, suggesting a higher sp^3 content in the latter film.

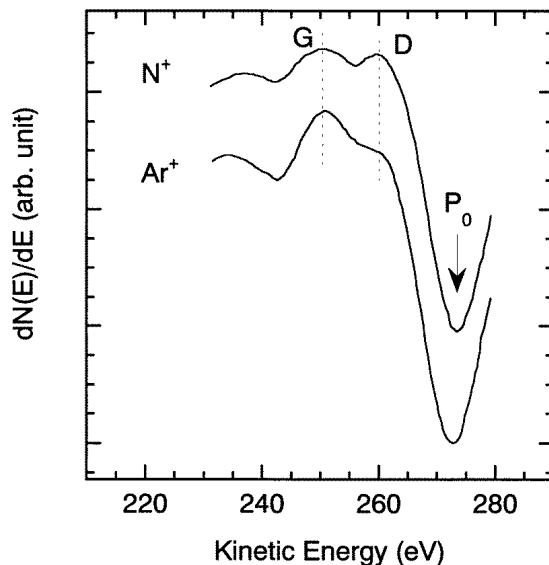


Figure 1. AES spectra of the carbon films prepared on $\text{Al}_2\text{O}_3(0001)$ substrates by sputtering a graphite target with 3 keV Ar^+ and N^+ ions.

The dependence of the structure on which sputtering ions were used was also observed for three films via Raman analysis. Figure 2 compares the Raman spectra of the carbon films. The Raman spectra were obtained using micro-Raman spectroscopy using a 514 nm Ar^+ laser as the excitation source. One sees that the Raman spectra of the N^+ - and CH_4^+ -sputtered films are similar and are quite different from that of the film produced by Ar^+ -ion sputtering. The Raman spectra of N^+ - and CH_4^+ -sputtered films are symmetrical and are quite broad, while that of the Ar^+ -sputtered film obviously consists of two peaks. From the literature it is known that the Raman spectra of diamond-like carbon films of high sp^3 content can be well fitted by

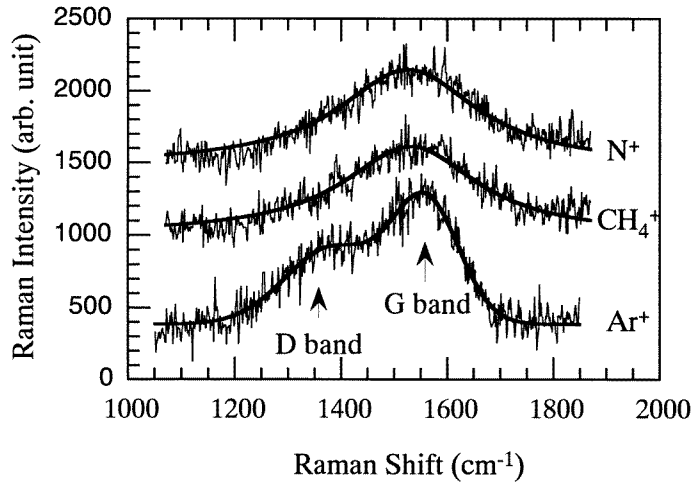


Figure 2. Comparison of the Raman spectra of the films prepared by sputtering with 3 keV Ar⁺, CH₄⁺, and N⁺ ions.

a single peak using the Breit–Wigner–Fano (BWF) line shape described by

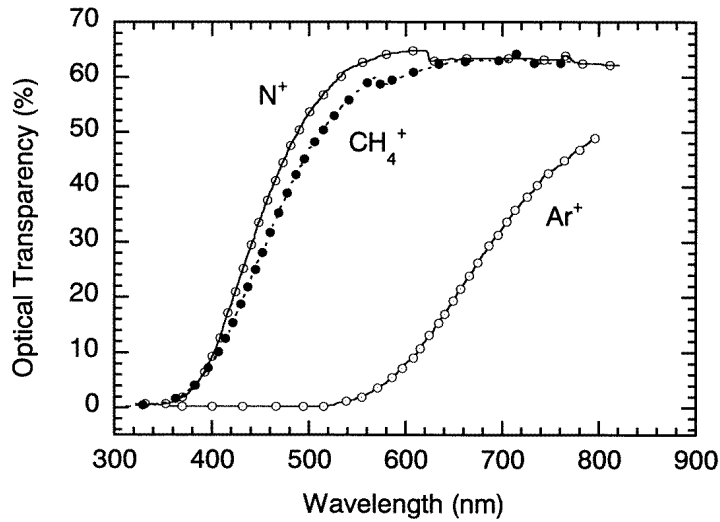
$$I(\omega) = \frac{I_0[1 + 2(\omega - \omega_0)/Q\Gamma]^2}{1 + [2(\omega - \omega_0)/\Gamma]^2}. \quad (1)$$

In this formula, $I(\omega)$ is the signal intensity as a function of the frequency ω , I_0 is the peak intensity, ω_0 and Γ are respectively the peak position and the full width at half-maximum, and Q is a coupling coefficient which is sensitive to the sp^3 content in the film [17]. Using the BWF line shape, Raman spectra of the N⁺- and CH₄⁺-sputtered films can be well fitted by a single peak centred at about 1555 cm⁻¹ with a Q -value of about -10 , which suggests an sp^3 fraction no less than 40% in the two films [17]. The Raman spectrum of the Ar⁺-sputtered film consists obviously of two peaks and cannot be fitted by a single peak with the BWF line shape. Instead, it can be fitted by two Gaussian peaks at about 1383 and 1560 cm⁻¹ corresponding respectively to the D and G lines of graphite. The intensity ratio of the D and G lines is calculated to be about $I(D)/I(G) = 0.885$. This indicates that the Ar⁺-sputtered film has a higher sp^2 content than the N⁺- and CH₄⁺-sputtered films.

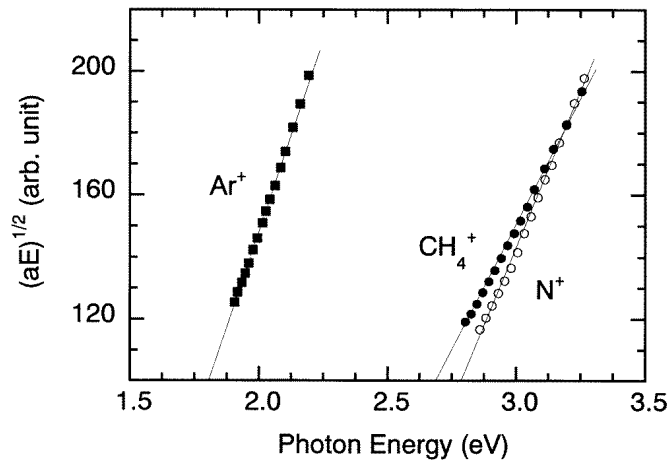
Both AES and Raman analysis demonstrate a structure dependence of the films on which sputtering ions were used, which, in general, should result in different properties. The optical properties of the three films were thus examined by optical spectroscopy in the visible and ultra-violet range. Figure 3(a) plots the optical transparencies of the three carbon films as functions of the wavelength. One sees from the figure that, in comparison with those of the N⁺- and CH₄⁺-sputtered films, the absorption edge of the Ar⁺-sputtered film shifted to the long-wavelength (low-photon-energy) side, indicating a difference in optical band gap of the three films. The optical band gaps of the three films can be determined from the spectra using the Tauc relationship

$$\alpha E \propto (E - E_B)^2$$

where α is the absorption coefficient, E is the photon energy, and E_B is the optical band gap. Figure 3(b) shows the values of $(\alpha E)^{1/2}$ for the three films as functions of the photon energy E . Using linear fits, the optical band gaps of the three films were estimated to be 1.42, 2.10, and 2.30 eV. Obviously, the optical band gaps of the N⁺- and CH₄⁺-sputtered films are



(a)



(b)

Figure 3. (a) Optical transmission and (b) $(\alpha E)^{1/2}$, for three films prepared by means of 3 keV Ar^+ -ion, CH_4^+ -ion, and N^+ -ion sputtering.

much larger than that of the Ar^+ -sputtered film. This supports the AES and Raman analysis in indicating that the films obtained by CH_4^+ and N^+ sputtering contain higher sp^3 contents than the Ar^+ -sputtered film.

The thermal stability of two films sputtered with N^+ and CH_4^+ ions was examined also by measuring the IR transparency at elevated temperatures. Figure 4 shows the IR transparency of the N^+ -sputtered film as a function of the annealing temperature. Similar results were also obtained for the CH_4^+ -sputtered one. One sees that over the annealing temperature range the IR transparency of the films did not change much. When the films were cooled down to room temperature, their IR transparency was recovered. This suggests that the two films are quite against heating.

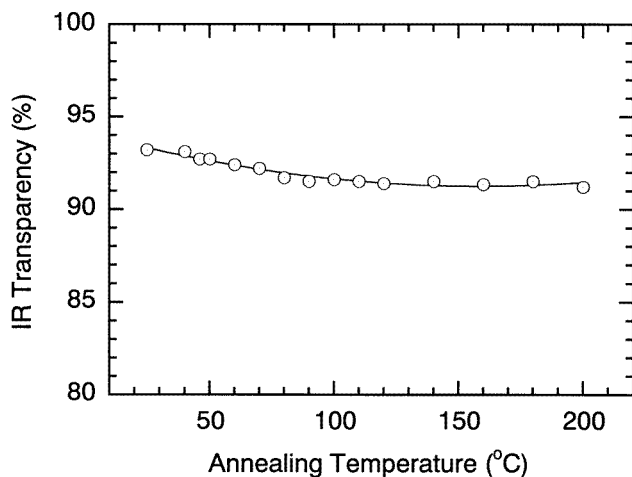


Figure 4. The IR transparency of the N^+ -sputtering film as a function of the annealing temperature. The line is a guide to the eye.

In summary, diamond-like carbon films have been prepared using different sputtering ions. The structure and properties of the carbon films were dependent on which sputtering ions were used.

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