NITROGEN AND ALUMINUM DOPED DIAMOND-LIKE CARBON THIN FILMS BY DC MAGNETRON SPUTTERING DEPOSITION

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Abstract

Diamond-like carbon (DLC) thin films used in this study were prepared with DC magnetron sputtering deposition. Silicon (100) wafers were used as the substrates onto which an RF bias was applied during the film deposition. For the nitrogen doped DLC films, a pure graphite target was used as the carbon source and nitrogen gas was introduced into the deposition chamber via a mass flow controller. For the aluminum doped DLC films, the graphite and a pure Al targets were co-sputtered. Nitrogen doping level was monitored by controlling the N_2 flow rate from 0 to 12 sccm, while Al doping level was controlled by varying the DC power from 0 to 25 W applied on the Al target. All the DLC films were deposited at room temperature (~22°C). The DLC films lightly doped with nitrogen and aluminum could maintain the high sp^3 contents in the films indicating good mechanical properties of these films.

Keywords: Diamond-like carbon; Nitrogen doping; Aluminum doping; DC magnetron sputtering.

1. Introduction

Diamond-like carbon (DLC) thin films have been studied for their growth, structure, properties, and applications. The great versatility of carbon materials arises from the strong dependence of their properties on the ratio of sp^2 (graphitelike) to sp^3 (diamondlike) bonds. In DLC films, sp^3 bonds are responsible for the mechanical properties, whereas sp^2 bonds, which lie near the Fermi level, control the optical and electronic properties of the films. Although DLC exhibits many desirable characteristics for several applications, its properties can be further modified or improved by the introduction of nitrogen and some other elements including Au, Cr, Fe, Cu, Nb, Ni, Si, Sn, Ta, Ti and W. Amorphous carbon films with nitrogen doping have been studied mainly for three aspects: (i) the electronic doping of a-C with nitrogen [1,2], (ii) the incorporation of a small concentration of nitrogen to release high stress of a-C [3,4], and (iii) the synthesis of superhard compounds [5,6]. Usually, only a few atomic percentage of nitrogen was incorporated into DLC films. Sputtering carbon in the presence of nitrogen (N_2) gas typically produces amorphous nitrogenated carbon (a-C:N) films. The actual behavior of nitrogen is complicated because of the presence of both sp^3 and sp^2 bonding. It was reported that nitrogenated carbon films can have a better friction behavior than hydrogenated carbon films [5]. The incorporated N_2 could lead to formation of C=N and C≡N bonds which at the same time create unsaturated spins and mid-gap states resulting in a substantial decrease of electrical resistance of the DLC film [6]. The properties of carbon films can also be changed by incorporating Al in the films [7].

This paper studies the effects of doping nitrogen and aluminum into diamond-like carbon (DLC) thin films by DC magnetron sputtering on the structural properties of the films in terms of N_2 flow rate and Al target power during film deposition.

2. Experimental Details

DLC films were deposited on Si (100) substrates with a DC magnetron sputtering system (Penta Vacuum). A 3-inch graphite target (99.995% C) and a 3-inch Aluminum target (99.995% Al) were used as C and Al sources. An RF bias was applied to the substrate during the film deposition. Nitrogen doping level was monitored by controlling the N_2 flow rate from 0 to 12 sccm, while Al doping level was controlled by varying the DC power from 0 to 25 W applied on the Al target. All the DLC films were deposited at room temperature (22°C).

The structural properties were characterized by means of Raman Spectroscopy (Renishaw S2000) using a 633 nm HeNe laser at 2 mW over the range of 800-2000 cm^{-1} and X-ray Photoelectron Spectroscopy (XPS) (Ultra, Kratos) with Al monochromatic X-ray radiation (15 kV and 10 mA). XPS was also used to determine the film elemental composition. For calibration, a standard HOPG graphite sample was also measured with XPS showing a binding energy of 284.3 eV and an FWHM of 0.4 eV.

3. Results and Discussion

A DLC C 1s core level XPS spectrum is composed of at least two components, i.e. sp^2 and sp^3 components with the binding energies of 284.4 eV and 285.2 eV, respectively.

Fig. 1 shows the Raman spectra of the DLC:N films deposited with the N_2 flow rate from 1 to 12 sccm. Each spectrum is deconvoluted into two peaks with Gaussian line shapes, i.e. D and G bands, respectively. With the increase of N_2 flow rate, the D peak becomes stronger, which means more pronounced graphitization of the DLC:N films.

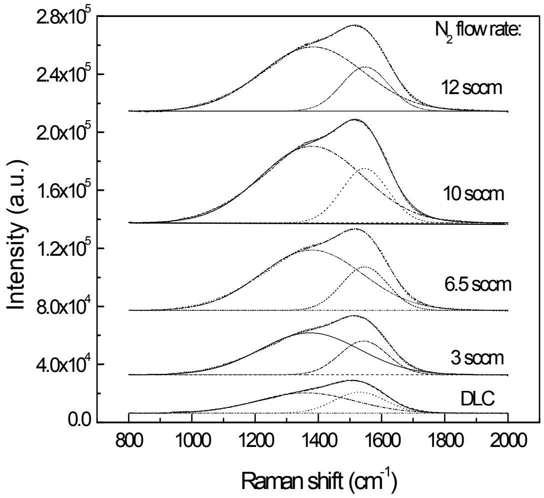
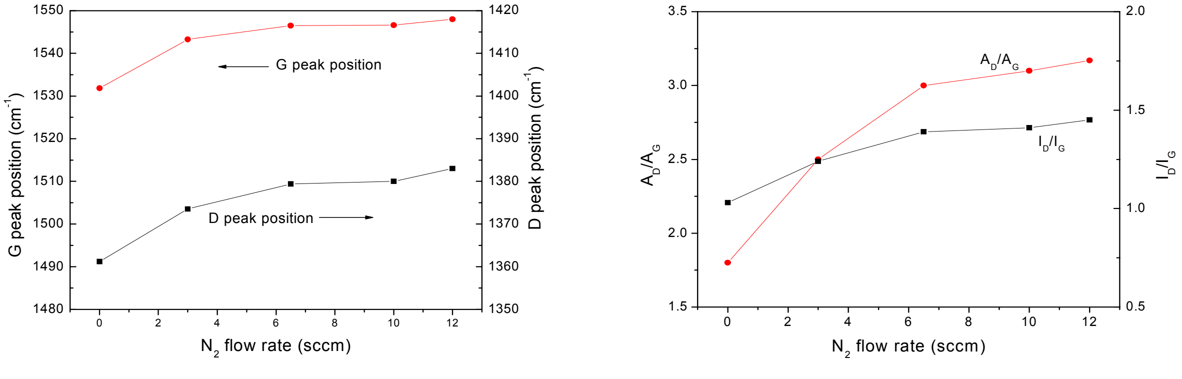


Fig. 1 Raman spectra of DLC:N films deposited at different N_2 flow rates.

The fitting parameters of the Raman spectra are shown in Fig. 2, including D and G peak positions, peak intensity ratios (I_D/I_G) and integrated area ratios (A_D/A_G). Both blue shifts (to higher wave numbers) of D and G peak positions (Fig. 2 (a)) and increases in I_D/I_G and A_D/A_G (Fig. 2 (b)) illustrate decreases in both disorder and bond angle of the DLC:N films.



(a) (b)

Fig. 2 Raman peak information of DLC:N films with respect to N_2 flow rate: (a) D and G peak positions and (b) I_D/I_G and A_D/A_G ratios.

The nitrogen contents of the DLC:N films are determined with XPS N 1s spectra, while the sp^3 contents of the films are determined with XPS C 1s spectra using the sp^3 peak area over the overall C 1s band area from each C 1s spectrum as shown in Table 1. With the increase of nitrogen flow rate, the sp^3 content decreases from 44.8% to 30.1%.

Table 1. Nitrogen and sp^3 contents in sputtered DLC:N films.

N_2 flow rate (sccm)	0	3	6.5	10	12
N content (at.%)	0	5.7	8.7	9.3	10.1
sp^3 content (%)	44.8	37.3	35.3	32.4	30.1

Aluminum was co-sputtered with powers of 5, 10, 15 and 25 W applied on the Al target during the DLC:Al film deposition. The Al contents in the DLC:Al films are also evaluated with XPS spectra as tabulated in Table 2. The Raman spectra of the DLC:Al films are illustrated in Fig. 3 with the peak positions and the intensity and area ratios plotted in Fig. 4. Both the D and the G peaks shift to higher wave numbers and the I_D/I_G and A_D/A_G ratios increase with the increase of Al content in the DLC:Al films. From Table 2, it can be seen that the sp^3 content decreases as the power on the Al target increases.

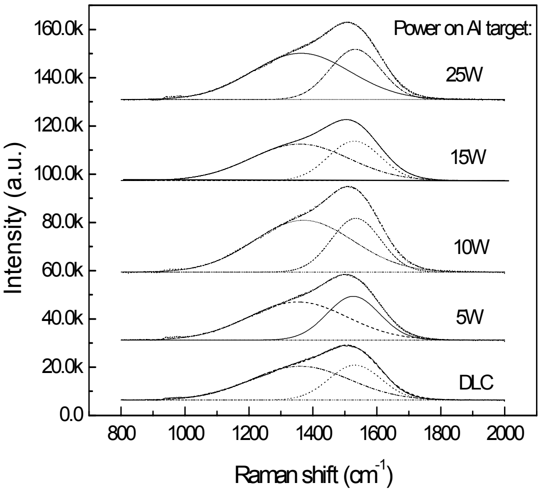
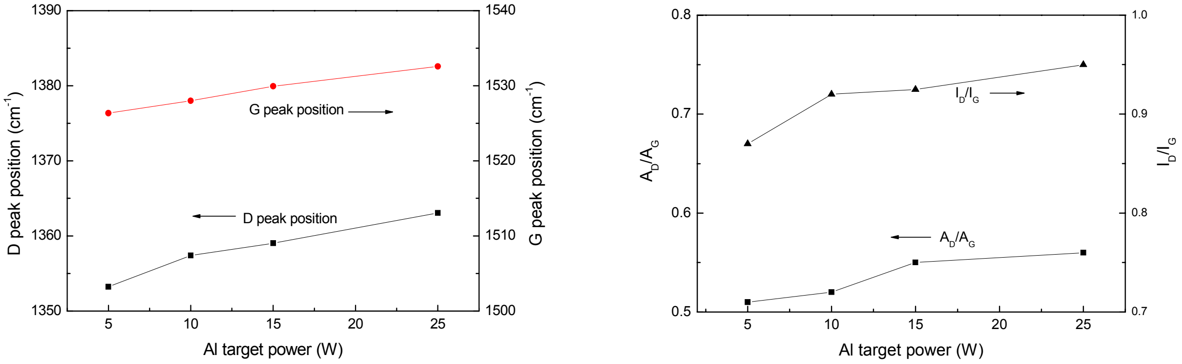


Fig. 3 Raman spectra of DLC:Al films deposited at different sputtering powers.



(a) (b)

Fig. 4 Raman peak information of DLC:Al films: (a) D and G peak positions and (b) I_D/I_G and A_D/A_G ratios.

Table 2. Al and sp^3 contents in sputtered DLC:Al films.

Al target power (W)	0	5	10	15	25
Al content (at.%)	0	0.9	2.0	2.4	3.1
sp^3 content (%)	44.8	43.1	42.08	31.8	30

4. Conclusions

- DLC films doped with nitrogen and aluminum were produced with DC magnetron sputtering deposition.
- With increase of nitrogen flow rate from 0 to 12 sccm during the film deposition, the sp^3 content in the DLC:N films decreased from 44.8% to 30.1%, while the nitrogen content in the films increased from 0 to 10.1 at.%.
- The sp^3 content of the DLC:Al films decreased from 44.8% to 30% with the increase of aluminum content from 0 to 3.1 at.% in the films, when the sputtering power on the Al target was increased from 0 to 25 W.

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