

Properties of N-doped Diamond-like Carbon Films Prepared by the PLD Method

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N-doped diamond-like carbon (DLC) films were deposited on Si substrates by pulsed laser deposition (PLD) at varying N_2 pressure. The films were characterized by Raman spectroscopy and X-ray diffraction (XRD). Spectra show that the sp^2 hybridized carbon content increases with increasing N_2 pressure and that the films have a mainly amorphous structure. The residual stress of the films is reduced from 31.8 to -2.2 GPa by N-doping at appropriate N_2 pressure.

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Diamond-like carbon (DLC) films have many superior properties, including mechanical hardness, dielectric strength, chemical inertness, low coefficient of friction, and optical transparency in the infrared ranges, making them promising for a wide range of applications [1, 2]. They can be synthesized by a variety of methods, including pulsed laser deposition (PLD) [2, 3] and, under some conditions, filtered cathodic vacuum arc (FCVA) deposition [4]. DLC properties approach those of crystalline diamond. However, the films have very high intrinsic stress [5, 6] and consequently tend to exhibit low adhesion with increased thickness [5, 6], thus severely limiting their practical applications.

Alloying amorphous carbon (a-C) films with transition metals such as Ni, Co, Ti, Mo, and W is a common strategy for reducing residual stress in DLC films [7]. The effects of dopants such as B, P, and N on the microstructure, electrical structure, and mechanical and optical properties of a-C films have been studied. However, there has been no extensive study on the effect of nitrogen concentration on the properties of N-doped DLC films.

In this work, we prepared N-doped DLC films by PLD at varying N_2 pressure. We then investigated the structure and residual stress of the films by Raman spectroscopy and X-ray diffraction (XRD).

N-doped diamond-like carbon films were deposited on Si wafers by PLD at room temperature. The distance between target and substrate was 4 cm. The excimer laser energy density was 7.5 J/cm^2 . Nitrogen pressure was in the range $8\text{-}20 \times 10^{-3}$ Pa.

The crystal structures and residual stresses of the films were determined by X-ray diffraction (X Pert PRO) us-

ing $\text{Cu K}\alpha$ radiation with an incidence angle of 0.5° and a scanning resolution of 0.02° . The structures were further analyzed by visible Raman spectroscopy (Renishaw) with Ar laser (514.5 nm). Spectra were recorded in the $900\text{-}2500 \text{ cm}^{-1}$ range. All film thicknesses were about 500 nm , as determined by cross-section scanning electron microscopy (SEM).

Figure 1 shows Raman spectra of the films deposited at varying N_2 pressure. Broad asymmetric bands are evident between 1000 and 1800 cm^{-1} , similar to those for DLC [2], indicating that the diamond-like phase predominates in the films. The spectra can be deconvoluted into

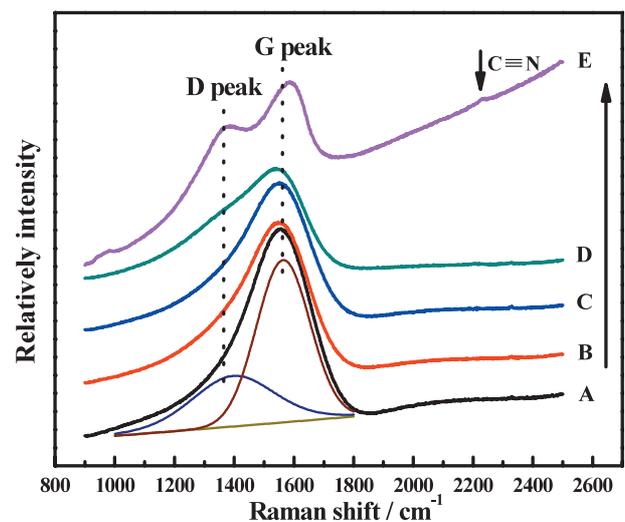
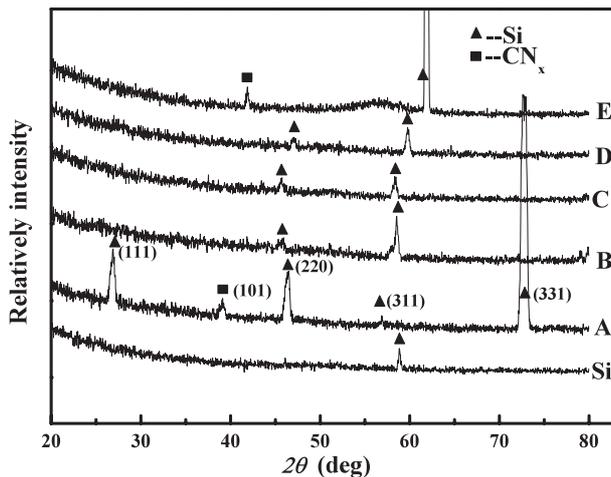


Fig. 1 Raman spectra of the films at varying N_2 pressure (Pa): (a) 8.0×10^{-3} ; (b) 6.0×10^{-2} ; (c) 2.5×10^{-1} ; (d) 2.8; (e) 20.

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Table 1 Raman data and residual stresses of DLC: N films

Sample	N ₂ pressure (Pa)	G peaks Position (cm ⁻¹)	D peaks Position (cm ⁻¹)	I _D /I _G	σ (GPa)
A	8.0 × 10 ⁻³	1561	1390	0.54	-14.2
B	6.0 × 10 ⁻²	1560	1393	0.77	-2.2
C	2.5 × 10 ⁻¹	1559	1392	0.75	-3.5
D	2.8 × 10 ⁰	1557	1387	1.52	9.1
E	2.0 × 10 ¹	1579	1369	-	31.8

Fig. 2 GIXRD spectra of the films at varying N₂ pressure (as for Fig. 1).

two Raman active bands: D (disorder) and G (graphitic) bands [2, 6]. All peak-fitting parameters were obtained by mixing Gaussian and Lorentzian shapes and linear backgrounds. The G band is attributed to the stretching-vibration mode of any pair of sp² sites, both in C=C chains and aromatic rings. The D band is attributed to the breathing mode of sp² sites in aromatic rings only [1].

Table 1 shows changes in the ratio of D-band to G-band intensity (I_D/I_G) and the residual stress σ at varying N₂ pressure. The ratio increases with increasing pressure, indicating that the relative concentration of sp² atoms increases in the films. The D and G bands shift a little with changing N₂ pressure. In addition, as shown in Fig. 1, weak peaks at around 2230 cm⁻¹ correspond to C ≡ N [8] bonds, implying that the degree of C ≡ N bonding is very

small compared with the degree of carbon-carbon bonding.

Figure 2 shows glancing-incidence XRD (GIXRD) spectra of the films deposited on Si substrates at varying N₂ partial pressure. No significant diffraction peaks other than for the Si substrate are observed for all films, indicating that the films have a mainly amorphous structure. However, obvious peaks at 2θ = 40.04° for samples A and E may correspond to formation of a CN_x phase. Residual stress is determined by measuring the shift in Si-substrate diffraction peak before and after deposition and then calculating quantitatively by the following equation [9]

$$\sigma = \frac{E d_n / \cos(\theta_n - \alpha) - d_0 / \cos(\theta_0 - \alpha)}{\nu d_0 / \cos(\theta_0 - \alpha)}, \quad (1)$$

where E , ν , d_n , θ , and α are the Young's modulus, Poisson's ratio, d -spacing for (hkl) planes, and X-ray diffraction and incidence angles, respectively. The residual stresses of the films are summarized in Table 1. Stress has been reduced from 31.8 to -2.2 GPa by N-doping at appropriate N₂ partial pressure.

N-doped diamond-like carbon films have been deposited by PLD at varying N₂ pressure. Raman spectra studies show that the sp² hybridized carbon content increases with increasing N₂ pressure. XRD studies show that the films have a mainly amorphous structure and that the residual stress of the films is reduced to -2.2 GPa by N-doping at appropriate N₂ partial pressure.

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