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Effects of nitrogen incorporation on structure of a-C:H films deposited on polycarbonate by plasma CVD

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Abstract

Nitrogen-incorporated-hydrogenated amorphous carbon (a-C:H:N) films were deposited on polycarbonate (PC) substrates by r.f. plasma-enhanced chemical vapor deposition (PECVD). Effects of nitrogen incorporation on microstructure, bonding states, chemical composition, internal stresses, and friction coefficients of deposited films were investigated. The films were characterized by X-ray photoelectron microscopy, infrared microscopy (IR), Raman spectroscopy and friction tests. Results from the measurement indicate that incorporated nitrogen content has considerable effects on film properties. Raman spectra of the a-C:H:N films are broad, asymmetric and centered at around wavenumber of 1500 cm^{-1}. Shifting of the G-peak toward the higher wavenumber, narrower bandwidth of the G-peak and an increase of the I_D/I_G ratio demonstrate the graphitic character of the a-C:H:N films with the further increase of the atomic fraction of nitrogen (N/C). IR spectra demonstrate nitrogen bonded to carbon and hydrogen as C$\equiv$N, C$=$N, N–H and C–H bonding configurations in the a-C:H:N films. The internal stress considerably decreased as well as the friction coefficient is low when the N/C fraction increased. The surface roughness of the a-C:H:N films estimated by atomic force microscopy (AFM) seems to be less smooth with the increase in the N/C fraction.
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1. Introduction

Plastics have become important materials because they can be produced in large scale and are cheaper and lighter than many other materials. Among them, polycarbonate (PC) is well-known, commercially available materials. Owing to its excellent breakage resistance, PC has replaced glasses in many applications, such as automobile headlamps, safety shield of window and ophthalmic lenses. However, PC is still limited to non-abrasive and chemical-free environments due to its low hardness, low scratching resistance and high susceptibility to chemical attacks. To overcome this limitation, PC coated by hydrogenated amorphous carbon films has been studied in recent years [1,2].

Hydrogenated amorphous carbon (a-C:H) have very attractive properties such as high hardness, infrared trans-

parency, chemical inertness, low friction coefficients, and biocompatibility. Owing to their unique properties, a-C:H films, either in polymer-like phase or as diamond-like phase, have been deposited on plastics. They have also found a wide range of technological applications as protective coating of plastic optical components [3], protecting flexible packaging from gas and water vapor permeation [4]. However, weak adhesion and delamination from plastic substrates, arising from high internal compressive stress of a-C: H films, are main factors to limit film thickness and their durability over time.

Two possible approaches to reduce the internal stress in a-C:H films can be performed. One is the increase in the self-bias resulting in high-energy particles which collide with substrate surface. The other is the structural modification of a-C:H films by the addition of some elements to hydrocarbon precursors, such as nitrogen or silicon. In both cases, these effects induce a-C:H films to be more graphitic. It results in lower internal stresses, and sometimes, in lower

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hardness [5]. No papers concerning to the reduction of internal stresses in a-C:H films deposited on plastics, especially on PC, have been reported so far.

In this paper, nitrogen-incorporated a-C:H films (denoted as a-C:H:N) were grown on PC from a mixture of N_2/CH_4 binary gases using r.f. plasma-enhanced chemical vapor deposition (PECVD). Effects of the nitrogen incorporation on microstructure, internal stresses, and friction coefficients of deposited films were examined. Characterization of bonding states and film quality were performed by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Reduction of internal stress was determined as a function of the nitrogen atomic fraction (N/C). The friction coefficient as well as the surface topography of a-C:H:N films related to the N/C fraction were estimated by friction tests and atomic force microscopy (AFM), respectively.

2. Experimental procedures

a-C:H:N films were deposited on PC of 0.5 mm in thickness by plasma decomposition of methane /nitrogen (CH_4/N_2) gases. A nitrogen fraction of the flow rate is defined as $N_2/(N_2+CH_4)$, ranging from 0% to 50%. Film deposition was performed in a 13.56-MHz parallel-plate capacitively coupled plasma reactor. A polycarbonate substrate, mounted on the r.f. powered electrode, was kept less than 80 °C during a plasma deposition by the feedback-cooling system. Prior to the film deposition, the PC substrate was bombarded in argon plasma up to 5 min in order to eliminate any impurity and to generate radicals on the substrate surface. The rf-power density and gas-pressure were set constantly at 1.7 W/cm^2 and 26.6 Pa, respectively, during the film growth.

Information about chemical bonding and elemental composition of the deposited films was determined by XPS measurement, carried out in a Kratos ESCA-3300 spectrometer, employing Mg Kα (1253.6 eV) X-ray source. All spectra were measured at a voltage of 8 kV, current of 30 mA, and pass energy of 32 eV with step energy of 0.1 eV. A nitrogen atomic fraction of deposited films, defined as a fraction (N/C), was calculated using peak area and the appropriate sensitivity factors for nitrogen and carbon. Raman spectra were detected on a Renishaw Raman spectrometer employing He/Ne ion laser with the light wavelength of 632.8 nm as the excitation source. All samples were detected at ambient temperature and the exposure time of 10 min. Ten scans with the spectral resolution of 1 cm^{-1} in the range of 800–2000 cm^{-1} were performed and their values were averaged. Infrared spectroscopy was used to probe the local chemical bond configuration in a-C:H:N films. Infrared microscopy (IR) data in a reflective mode were collected from a-C:H:N films of about 500 nm in thickness on a Thermo-Nicollet AVATAR 360 instrument. All spectra were detected in the range of 4000–

600 cm^{-1} with 250 scans at spectral resolution of 8 cm^{-1}. Absorption spectra of a-C:H:N films were obtained by the subtraction of a spectrum of a blank PC.

Thickness and curvature of the film-coated substrate were determined using a KLA Tencor P.15 profilometer in order to estimate internal residual compressive stress.

Surface roughness of the a-C:H films was estimated by Nano-Scope III AFM (Digital Instrument) operating in the tapping mode under ambient conditions, employing a cantilever and a silicon tip. As the reference, the surface of a blank PC was measured together with the surface of the deposited films.

Friction measurement was performed on the films coated on PC using a dry sliding tribometer. Frictional tests were conducted in ambient conditions under a load of 0.5N with a sliding speed of 20 mm s^{-1} through the steel ball (ASTM 52100) of 4.8 mm in diameter for an hour with the humidity up to 25%.

3. Results and discussion

3.1. FTIR characterization

The variation of nitrogen bonded to C and H, determined from the infrared spectra of both a-C:H and a-C:H:N films with different N/C fractions, is shown in Fig 1. The weak absorption of the spectrum having the N/C fraction of 6.8% can be seen at around 2210 cm^{-1} assigned to the C≡N stretching mode. The C≡N absorption is the obvious indication of incorporated nitrogen atoms presented as terminal bond in the amorphous network. In addition, a singly bonded C−H stretching mode and a broad peak N−H centered at about 2920 and 3400 cm^{-1} were detected, respectively. The absorption of the C−H stretching mode decreased, whereas the intensities of the N−H and the C≡N stretching modes increased with increasing the N/C fraction.
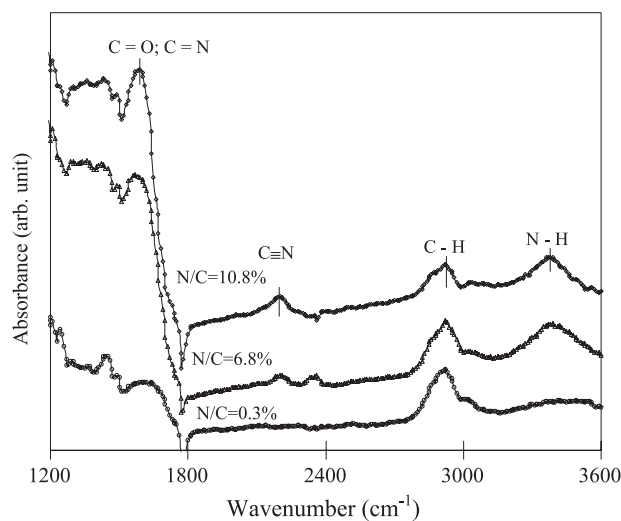

Fig. 1. FTIR spectra of a-C:H:N films showing the various bonding configurations of incorporated nitrogen.

Not being similar to these peaks mentioned above, C—N and C=N peaks were not clearly separated from the range between 1300 and 1700 cm^{-1}. A sharp peak located in the range of 1590–1600 cm^{-1} might be attributed to C=N or C=O. However, the oxygen atomic fraction, obtained from the XPS analysis, is slightly changed in about 7–8.5% for all a-C:H:N films, therefore, rapidly increased intensity of the peak at around 1600 cm^{-1} could be due to the incorporated nitrogen, resulting in the C=N absorption. Moreover, IR results provide evidence of incorporated atomic nitrogen, which substitutes atomic carbon in the carbon network of the a-C:H:N films. These absorption peaks are in good agreement with those reported in previous papers [5,8].

3.2. Raman spectroscopy

Typical Raman spectra of pure a-C:H and a-C:H:N films deposited from the various N/C fractions are shown in Fig. 2. All spectra appear as a single broad peak centered at about 1500 cm^{-1} with a small shoulder at around 1300 cm^{-1}. The spectra become broader and slightly shifted to a higher wavenumber side with the higher nitrogen content incorporated into the films. Using a Gaussian distribution and a linear background, each spectrum was deconvoluted into two components: one (D-peak) denotes disordered graphite and the other (G-peak) represents graphite-like sp^2-bonded carbon.

The G-peak position, the bandwidth of the G-peak and the intensity of D-peak to G-peak (I_D/I_G) ratio versus the N/C fraction are shown in Table 1. The G-peak position was shifted from 1503 to 1537 cm^{-1} whereas its bandwidth tapered off from 219 to 177 cm^{-1} corresponding to the N/C fraction increased from 0.3% to 10.8%. The intensity ratio of the D-peak to G-peak (I_D/I_G) is considerably increased from 0.76 to 2.35 with the further increase of the N/C fraction. Shifting of G-peak towards higher wavenumber,
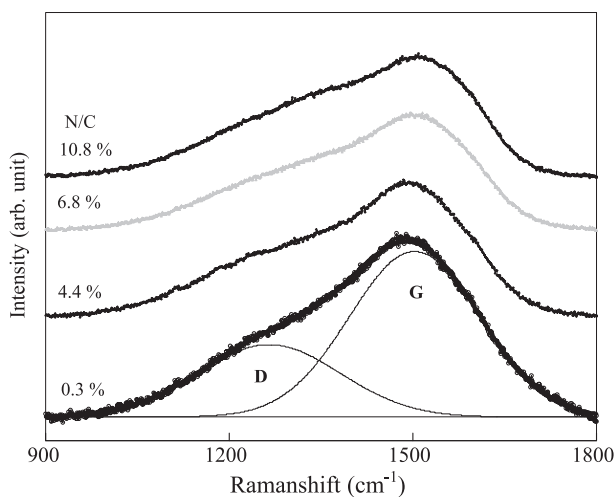
Table 1
G band position (a), G bandwidth (b) and I_D/I_G ratio (c) as a function of the N/C fraction in the a-C:H:N films

N/C (%)	D-position (cm^{-1})	FWHM (cm^{-1})	G-position (cm^{-1})	FWHM (cm^{-1})	I_D/I_G
0.3	1274	295	1503	219	0.76
4.4	1306	331	1515	205	1.04
6.8	1345	362	1527	192	1.58
10.8	1363	371	1537	177	2.35

narrower G-bandwidth and increasing the I_D/I_G ratio due to the enhancement of the N/C fraction brought about the more formation of sp^2 cluster sites correspondent to the increase in the structural disorder of the a-C:H:N films [6].

3.3. XPS characterization

The C1s and N1s peaks broaden and become more asymmetric with increasing nitrogen concentration in the films. These effects are a clear indication of nitrogen atoms involved in chemical bonds with carbon in three possible distinct chemical states: C–N, C=N, and C≡N [7]. The C1s peak corresponding to the N/C fraction of 10.8% was deconvoluted into four assignments using a Gaussian distribution (shown in Fig. 3a). These assignments, having binding energies of about 284.5, 285.5, 286.2, and 287.4 eV, are correspondent to pure carbon network, denoted as C–C, C=N, C–N or C≡N, and C–O bonded network, respectively. Similarly, N1s peak was also deconvoluted into three assignments correspondent to N–C or N≡C, N=C and N–O bond, which are situated at about 398.5, 399.5, and 400.5 eV (Fig. 3b). The full-width-at-half-maximum (FWHM) values of the deconvoluted peaks for both C1s and N1s spectra are about 1.7 eV for C–C, 1.6 eV for C–N, C=N, and 2.0 eV for C–O and N–O bonds. The C–N/C=N ratio, calculated from C1s and N1s spectra is also matching for all samples, and this ratio increases from 44% to 68% with growing the N/C fraction from 4.2% to 10.8%. These deconvoluted assignments are found to be in good agreement with the previous reports [6,7]. The C–O and N–O assignments are probably related to the incorporation of oxygen into the films due to their exposure to the atmosphere prior to the XPS analysis.

3.4. Internal stress determination

The total internal stress is composed of two components: one is intrinsic stress produced during the deposition process, and the other is thermal stress arising from the difference in thermal expansion coefficients between the deposited film and the PC substrate. The intrinsic stress can be expressed by the Stoney's equation:

$$\sigma = \frac{E_p t_p^2}{6(1 - v_p) t_f} \left(\frac{1}{R} - \frac{1}{R_0} \right)$$

where E_p, v_p and t_p are Young's modulus (E_p=2.5 GPa, Poisson ratio (v_p=0.35), and the thickness of the PC

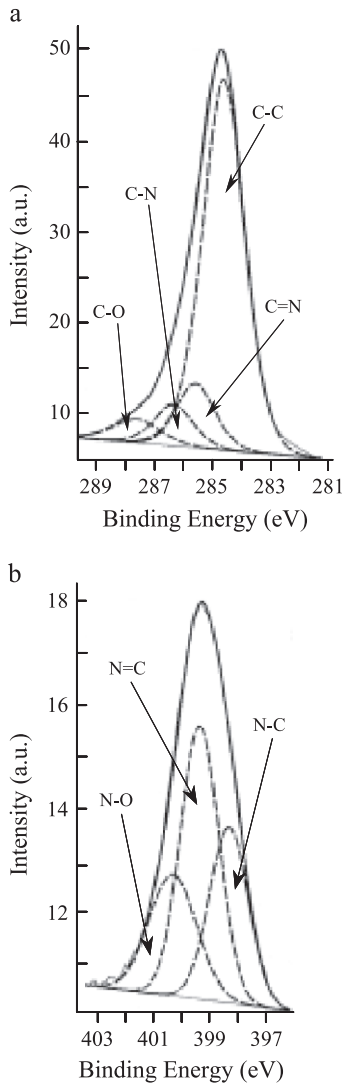Fig. 2. Raman spectra of a-C:H:N films with the different N/C fraction. Two assignments, the D-peak and G-peak at about 1300 and 1525 cm^{-1}, respectively.

a

Fig. 4. Internal stress vs. the N/C fraction in a-C:H:N films.

b

Fig. 3. Deconvoluted C1s and N1s spectra of a-C:H films having the N/C fraction of 10.8%.

with N–H bonds resulting in the reduction of the average coordination number and the overconstraining in the a-C:H:N films [5]. The considerable decrease in the internal stress owing to the nitrogen incorporation would be able to improve adhesion and prevent delamination of a-C:H:N films from a PC substrate. This also suggests that a-C:H:N films can be deposited more thickly or used as an interlayer between pure a-C:H films and PC substrate.

3.5. Tribological performance

Friction data of the a-C:H:N films with the different N/C fraction are presented in Fig. 5. The friction coefficient of a-C:H:N films was about 0.35 at the N/C fraction of 6.8%, and it decreased to 0.28 when the N/C fraction reached to 10.8%. The friction coefficients of the a-C:H:N films are lower compared to those of a bare PC and pure a-C:H films being approximate 0.7 and 0.43, respectively. Lower friction coefficients with increasing the incorporated-nitrogen content are attributed to the enlargement of

substrate (t_p=0.5 mm), respectively. R and R_0 are the spherical radii of the curvature of the film-coated PC and blank PC, respectively. Furthermore, thermal stresses have to be considered because PC as well as other plastics is rather sensitive to heating deformation. The thermal stress can be estimated by the following equation [9]:

$$\sigma = E_f\left(\alpha_f - \alpha_p\right)\left(T_p - T_a\right)$$

where E_f is Young's modulus of the films, α_f and α_p are the thermal expansion coefficients of the films and the substrates, T_p and T_a are the temperature of the polycarbonate during the film deposition and the stress measurement, respectively. As being much smaller than the intrinsic stress, the thermal stress can be neglected [9,10]. Fig. 4 shows the internal stresses as a function of the N/C fraction. The stress considerably decreased from 2.5 to 0.4 GPa when the N/C fraction went up from 0.3% to 10.8%. The stress reduction of the a-C:H films is due to replacement of C–H
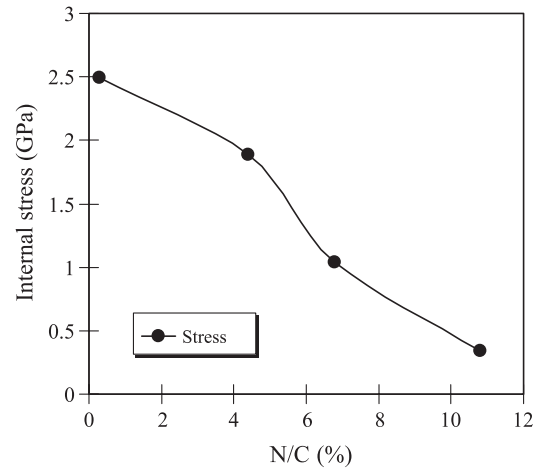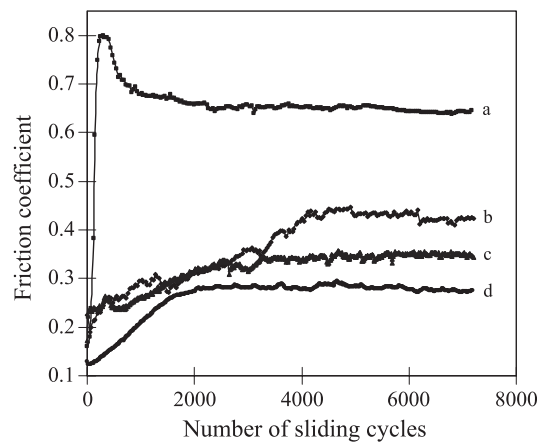

Fig. 5. Friction coefficient of a bare PC and a-C:H:N films with the different N/C fractions. (a) Friction coefficient of a bare PC; (b) of a-C:H; (c) of a-C:H:N films at the N/C=6.8%; (d) of a-C:H:N films at the N/C=10.8%.
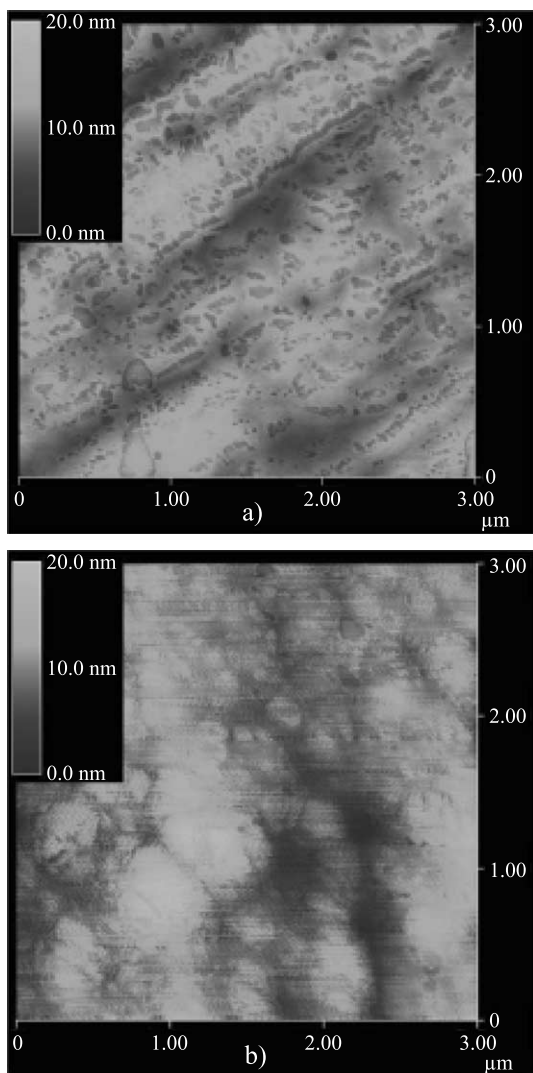
Fig. 6. 3-D topographical images of the a-C:H:N films (a) having the N/C fraction of 6.8%; (b) at the N/C fraction of 10.8%.

graphitic cluster size in a-C:H:N structure, which indicates that the deposited a-C:H:N film structure becomes enriched by sp^2 graphitic clusters working as a lubricant at the friction surface.

3.6. Surface roughness

AFM topography can provide more information about the film roughness. Fig. 6 illustrates 3-D topographical images (3×3 μm) of the films with the N/C fraction ranging from 6.8% and 10.8%. The results show that the surface morphology depends on the amount of nitrogen incorporated in the films. For the sample having the N/C fraction of 6.8% (Fig. 6a), the mean roughness (R_a) is less than 3.4 nm, and increases with increasing the amount of incorporated nitrogen (Fig. 6b). This is attributed to two main structural modifications in the a-C:H:N films: one is the increase in the number or the size of the graphitic domains (sp^2 carbon bonds) [11], and the other is the increase in the density of voids [12]. a-C:H:N films become slightly rougher whereas their friction coefficients decreased with the further nitrogen content incorporated. This is obvious evidence showing that the friction coefficient is rather affected by the number or the size of graphitic domain in the a-C:H:N films than their surface roughness.

4. Conclusions

a-C:H:N films were deposited on PC from the mixture of N_2/CH_4 gases by PECVD. The nitrogen incorporation affected the microstructure, chemical composition, bonding configuration as well as the internal stress and tribological properties of the deposited films. The XPS analysis shows nitrogen atomic fraction, N/C, increased from 0.3% in the pure a-C:H films to the 10.8% in the a-C:H:N films grown from the flow rate, $N_2/(N_2+CH_4)$, up to 50%. FTIR spectra show that incorporated nitrogen is bonded to carbon in the N–H, C=N and C≡N configurations. The a-C:H:N films become more graphitic and this resulted in the lower internal stress with increasing the N/C fraction. The considerable decrease in the internal stress due to the nitrogen incorporation suggests that the adhesion between the a-C:H:N films and PC substrate would be improved, and film thickness could be enhanced. The friction coefficient of the a-C:H films decreased whereas the surface roughness is slightly increased with the further nitrogen content incorporated.

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