

Spectroscopic analysis of photo-induced deformation of amorphous carbon nitride films

T Harata, M Aono, N Tamura, N Kitazawa and Y Watanabe

Department of Materials Science and Engineering, National Defense Academy,
Hashirimizu 1-10-20, Yokosuka, Kanagawa, 239-8686, Japan

E-mail: aono@nda.ac.jp

Abstract. Reversible photo-induced deformation of amorphous carbon nitride ($a\text{-CN}_x$) films was investigated. The films were deposited at 400 and 600 °C on a rectangular shaped ultrathin SiO_2 substrate by reactive radio frequency magnetron sputtering with graphite target and pure N_2 gas. The amount of deformation change was estimated from bending curvature of $a\text{-CN}_x/\text{SiO}_2$ bimorph structure. For the film deposited at 400 °C, it bent toward the film side under illumination. Photo-induced deformation of the film estimated from the bending angle was observed in the excitation energy of 1.77 to 3.35 eV. The maximum deformation was observed under illumination of 2.6 eV which corresponds with $\pi\text{-}\pi^*$ bond of carbon nitride. In contrast, the deformation was hardly observed in the films deposited at 600 °C. The difference in these two films was probably due to difference in sp^2 bonding and termination structures.

1. Introduction

Amorphous carbon nitride, $a\text{-CN}_x$, is a promising candidate coating material for blood contacting devices because of its good mechanical and biologically compatible properties, such as high hardness [1], low friction coefficient [1, 2] and biocompatibility [3]. Furthermore, $a\text{-CN}_x$ films behave as an n-type semiconductors. Thus, electrical and optical properties, such as low dielectric constant [4], electrical conductivity [5, 6], photoconductivity [5, 7, 8] and photoluminescence [9], were studied.

Recently, we revealed a reversible photo-induced deformation of $a\text{-CN}_x$ thin films prepared by reactive radio frequency magnetron sputtering [10]. The photo-induced deformation of $a\text{-CN}_x$ was observed as a bending of curvature of the ultrathin Si substrate under visible light irradiation [11]. In the future, the photo-induced deformation of $a\text{-CN}_x$ films will have great possibility to apply for devices which utilize the photo-mechanical conversion.

Photo-induced phenomena have also been reported on amorphous semiconductor and certain organic materials. In amorphous semiconductors, such as hydrogenated amorphous silicon ($a\text{-Si:H}$) and amorphous arsenic sulfide ($a\text{-As}_2\text{S}_3$), photo-induced volume changes and structural changes [12, 13] have been reported during past decades. These phenomena were not reversible. On the other hand, azobenzene-containing materials show the reversible change in shape as the photo-mechanical effect due to the photo-isomerization. Under UV light irradiation, the *trans* configuration of azobenzene is able to change into *cis* configuration. And then, the *cis* form will return to the *trans* form by irradiating visible light [14, 15]. The photo-isomerization of azobenzene also induce the changes of the size from 9.0 Å in the *trans* form to 5.5 Å in the *cis* form [15].



To elucidate the mechanism of the photo-induced deformation of a-CN_x films, it is worthwhile to study the dependence of deformation on the incident photon energy. Thus, in this study, we investigate spectroscopic features of the photo-induced deformation for the a-CN_x films deposited at two different temperatures, which show different structures.

2. Experimental

Amorphous carbon nitride, a-CN_x, thin films were prepared by reactive radio frequency (RF) magnetron sputtering. The target was graphite plate (purity 99.9999%) of 3 inches in diameter. The reactive gas was N₂ with the purity of 99.99%. N₂ gas flow and the pressure were kept constant at 3 sccm and 0.12 Torr, respectively. The RF power was 85 W. The a-CN_x films were deposited on rectangular shaped ultrathin substrates of SiO₂ glass. The size of the substrate was 30.0 x 2.0 x 0.05 mm³. The deposition temperature was fixed at 400 and 600 °C.

The amount of deformation change was estimated from the amount of bending for the a-CN_x films/substrate system. One end of the a-CN_x films/substrate was clamped and displacement of the other free end was measured by the optical-lever technique in dark and under illumination with visible light. A He-Ne laser (wavelength 632.8 nm) was used as the probe light, and the laser beam reflected on the free end of the specimen and then the laser spot was observed on the scale. A Xe lamp, 150 W, was used to irradiate the a-CN_x specimen with the spectroscopic light in the wavelength range of 370 to 700 nm, corresponding to the photon energy of 1.77 to 3.35 eV. The absorption coefficient spectra were obtained from the transmittance spectra using UV-vis-NIR spectrophotometer (JASCO, V-570). X-ray photoelectron spectroscopy, Raman spectroscopy and FT-IR spectroscopy were performed on the films to study the nitrogen concentration, the chemical bonding states and the film structures. XPS was operated using Mg K_α radiation under 10⁻⁹ Pa (Phi, ESCA 1600). The nitrogen concentration was evaluated from the area ratio of N_{1s} to C_{1s} core level peaks. Raman spectra were obtained using Nd-YAG laser with the wavelength of 532 nm (Seishin Trading, RA-07F). Infrared absorption spectra were obtained using Fourier transform infrared spectrometer (Thermo Scientific, NICOLET 6700) in the range of 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ and averaging over 64 scans.

3. Results and discussion

From the XPS analysis, the nitrogen concentration (N/C) of the films deposited at 400 and 600 °C was evaluated to be 0.50 and 0.32, respectively. Figure 1a shows the XPS N_{1s} spectra from each film. The N_{1s} spectrum can be decomposed into mainly two peaks; N-sp³C bonding state at 398.5 eV and N-sp²C bonding state at 400.0 eV. The intensity ratio of N-sp²C to N-sp³C bonds (N-sp²C/N-sp³C) of the films was calculated to be 0.62 (400 °C) and 0.65 (600 °C). Raman spectra were shown in figure 1b. The obtained spectra were similar to the typical one of amorphous carbon film [16], which indicates the existence of amorphous carbon network in the films. In addition, these two spectra are similar each other. A intensity ratio of D to G peaks (I_D/I_G) was 0.99 (400 °C) and 1.10 (600 °C). The I_D/I_G ratio decreases with decreasing cluster size L_a according to Ferrari [17]. In contrast, FT-IR spectra in 2100 to 2300 cm⁻¹ as shown in figure 1c, were different definitely. The absorption band at about 2200 cm⁻¹ indicates an existence of -C≡N and -N≡C bondings which are like termination structures.

From these results, it is found that the features of the film deposited at 400 °C are relatively high nitrogen concentration, low sp² bonding fraction, small cluster size, and existence of termination structures compared to the film deposited at 600 °C.

Figure 2 shows an absorption coefficient of the a-CN_x films deposited at 400 and 600 °C obtained from the transmittance spectra. The absorption coefficient of the samples prepared at 400 °C decreased slowly from approximately 2.8 eV. On the film deposited at 600 °C, the absorption coefficient gradually decreased in whole region. In the case of amorphous carbon nitride films, the absorption coefficient increases with increasing nitrogen concentration and decreasing sp² bonding fraction. We estimated the Urbach energy which corresponds to the width of the band tail and can be evaluated as the width of localization. A plot of ln[α(E)] versus photon energy should be linear, where α(E) is the absorption coefficient. The Urbach energy can be obtained from the slope of the straight line, and was

found to be 0.30 (400 °C) and 1.06 eV (600 °C). This means that the film deposited at 600 °C has high disordered structure compared to the film deposited at 400 °C.

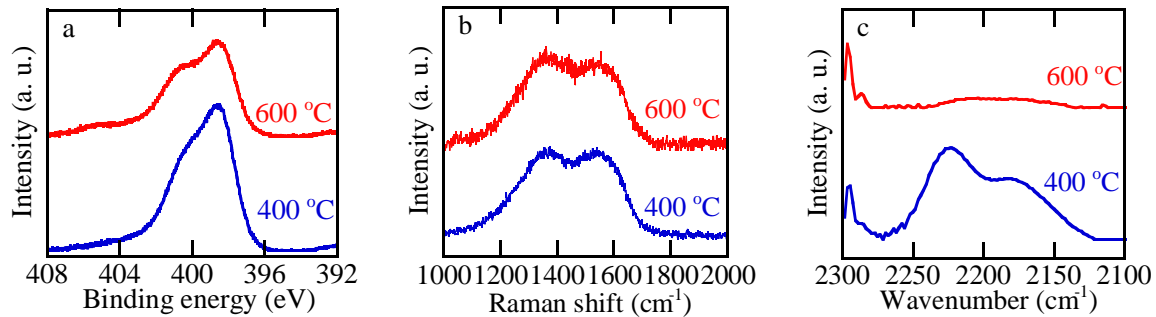


Figure 1. a) XPS N_{1s} spectra; b) Raman spectra; c) FT-IR spectra of the a- CN_x films deposited at 400 and 600 °C.

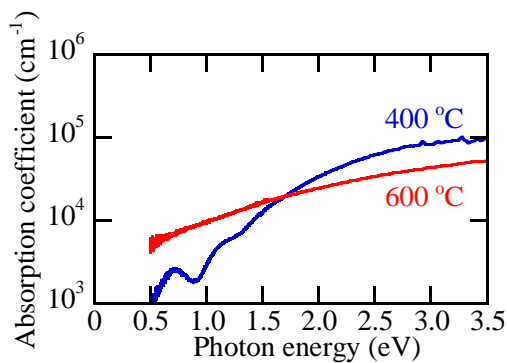


Figure 2. The absorption coefficient of a- CN_x films deposited at 400 and 600 °C.

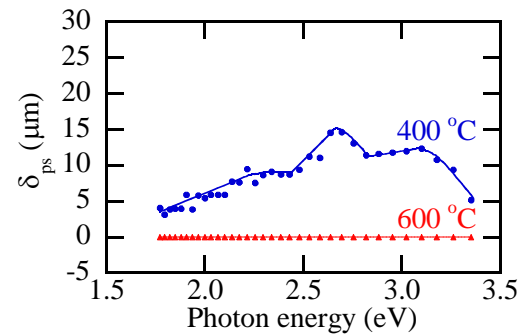


Figure 3. δ_{ps} as a function of incident photon energy. The solid lines are a guide for eyes.

Figure 3 shows a typical spectra of the amount of deformation (δ_{ps}) as a function of incident photon energy. The value of δ_{ps} was normalized by the incident light intensity. For the film deposited at 400 °C, the a- CN_x film/substrate system bent toward the film side when the incident light was irradiated from film side. And this deformation was observed reversibly against turning on and off the light. Moreover, the photo-induced deformation was observed in the whole region of the excitation photon energy (1.77 to 3.35 eV), which is related to the width of the localized states. The maximum value of δ_{ps} was discerned at the photon energy around 2.6 eV, which is close to $\pi-\pi^*$ band gap energy in graphitic C_3N_4 [18]. This suggests that the deformation mainly is induced by sp^2 C-N bond. On the other hand, δ_{ps} of the specimen deposited at 600 °C was below the detection limit of the present system in the whole region, and a total amount of the deformation under white illumination was almost zero.

Katsuno *et al.* [19] reported the spectrum of photoconductivity of sputtered a- CN_x film. A spectral shape of the photoconductivity at ~3.5 eV is similar to that of deformation obtained in this work. From this result, we surmise that both photoconductivity and photo-induced deformation simultaneously occur by photoexcitation between π and π^* states. We found that the ratio of photo to dark conductivity of the film deposited at 400 °C is 4.7, whereas in the case of the film deposited at 600 °C, it is approximately 100 [20]. We consider that photoconductivity and photo-induced deformation are competitive process and the former process is dominant in the film deposited at 600 °C. As described above, the film deposited at 600 °C has no termination structure, which behaves like traps of conduction electrons. Furthermore, high disordered structure and a large amount of sp^2 bonding can also contribute to high photoconductivity, because the sp^2 chain structures as conducting path increase with increasing the disorder [21]. From these results, we propose that the deformation is induced by

mainly sp^2 sites in the films and the existence of termination structure plays an important role for the deformation.

4. Conclusions

We investigated the spectroscopic analysis of photo-induced deformation of a-CN_x films in the range of 1.77 to 3.35 eV using optical-lever technique. The films were prepared on SiO₂ substrate by reactive radio frequency magnetron sputtering at the deposition temperatures of 400 and 600 °C. For the film deposited at 400 °C, the photo-induced deformation was observed in the whole range of the excitation energy. The maximum of the deformation was observed at about 2.6 eV. This energy is close to the π - π^* band gap of graphitic C₃N₄. On the other hand, the displacement of the specimen deposited at 600 °C was observed below detection limit of the measurement system.

Acknowledgements

The authors would like to thank Dr. Hisashi Miyazaki and Dr. Hiroaki Kishimura for useful discussion. This work was supported by JSPS KAKENHI Grant Number 26790054.

References

- [1] Hajek V, Rusnak K, Vlcek J, Martinu L and Haw-thorne H M 1997 *Wear* **213** 80
- [2] Wang P, Hirose M, Suzuki Y and Adachi K 2013 *Surf. Coat. Technol.* **221** 163
- [3] Cui F Z and Li D J 2000 *Surf. Coat. Technol.* **131** 481
- [4] Aono M, Naruse Y, Nitta S and Katsuno T 2001 *Diamond Relat. Mater.* **10** 1147
- [5] Takada N, Arai K, Nitta S and Nonomura S 1997 *Appl. Surf. Sci.* **113/114** 274
- [6] Tamura N, Aono M, Kishimura H, Kitazawa N and Watanabe Y 2012 *Jpn. J. Appl. Phys.* **51** 121401-1
- [7] Katsuno T, Nitta S, Habuchi H, Stolojan V and Silva S R P 2004 *Appl. Phys. Lett.* **85** 2803
- [8] Aono M, Goto T, Tamura N, Kitazawa N and Watanabe Y 2011 *Diamond Relat. Mater.* **20** 1208
- [9] Fanchini G, Ray S C and Tagliaferro A 2003 *Diamond Relat. Mater.* **12** 1084
- [10] Aono M, Harata T, Kitazawa N and Watanabe Y 2014 *Diamond Relat. Mater.* **41** 20
- [11] Harata T, Aono M, Kitazawa N and Watanabe Y Correlation of Photothermal Conversion on the Photo-induced Deformation of Amorphous Carbon Nitride Films Prepared by Reactive Sputtering *Appl. Phys. Lett.* under review
- [12] Gotoh T, Nonomura S, Nishio M, Masui N, Nitta S, Kondo M and Matsuda A 1998 *J. Non-Cryst. Solids* **227-230** 263
- [13] Tanaka K 1975 *Appl. Phys. Lett.* **26** 243
- [14] Barrett C J, Mamiya J, Yager K G and Ikeda T 2007 *Soft Matter* **3** 1249
- [15] Merio E and Ribagorda M 2012 *Beilstein J. Org. Chem.* **8** 1071
- [16] Ferrari A C 2002 *Diamond Relat. Mater.* **11** 1053
- [17] Ferrari A C 2000 *Phys. Rev. B* **61** 14095
- [18] Zhang J, Li Y, Zhu P, Huang D, Wu S, Cui Q and Zou G 2011 *Diamond Relat. Mater.* **20** 385
- [19] Katsuno T, Nitta S, Habuchi H, Iwasaki T, Itoh T and Nonomura S 2000 *Mat. Res. Soc. Symp. Proc.* **593** 499
- [20] Iwasaki C, Aono M, Tamura N, Kitazawa N and Watanabe Y 2012 *Jpn. J. Appl. Phys.* **51** 10NE26
- [21] Majumdar A, Das S C, Bogdanowicz R, Shripathi T, Langel W and Hippler R 2013 *Vib. Spectrosc.* **66** 63