

Formation of nanodots and nanostripes of carbon nitride on silicon by plasma and thermal treatments

Sang Hoon Kim, Ju-Hyung Hong* and Yoon-Bong Hahn†

School of Chemical Engineering and Technology, Nanomaterials Processing Research Center,
Chonbuk National University, Jeonju 561-756, Korea

*Korea Photonics Technology Institute, 459-3 Bonchon-dong, Buk-gu, Gwangju 500-460, Korea
(Received 26 April 2005 • accepted 14 November 2005)

Abstract—Amorphous carbon nitride (a-CN) films on Si(100) were grown by plasma-enhanced chemical vapor deposition at room temperature, followed by H₂ plasma and thermal annealing treatments, which produced densely and uniformly distributed nanodot- and nanostripe-like structures. The as-grown CN films showed two weak emission peaks at 2.1 and 2.4 eV, but the a-CN nanostructures showed a strong peak at 2.2 eV.

Key words: Amorphous Carbon Nitride, Nanostructures, PECVD, Thermal Annealing

INTRODUCTION

Recently, there has been considerable interest in carbon nitride thin films, because of their unique properties such as thermal conductivity, refractive index, high bonding strengths, chemical stability, optical property, wide band-gap energy [Lim et al., 1999; Xu et al., 2001]. The property of wide band-gap energy is utilized in optical devices, solar cells, and electric field emitters [Muhl and Mendez, 1999; Wei, 2001; Kim et al., 2004, 2005]. The carbon nitride films are also applied as coating materials because of high bonding strength [Lou et al., 1996; Takadom et al., 2003].

Various methods have been used for the deposition of carbon nitride films: bias-assisted hot filament chemical vapor deposition [Wang et al., 2000; Kundoo et al., 2003], electron cyclotron resonance chemical vapor deposition [Inoue et al., 1995], pulse laser ablation, ion beam deposition, and plasma enhanced chemical vapor deposition [Ju et al., 2001; Mutsukura, 2001; Yu et al., 2002]. Among these methods, plasma-enhanced chemical vapor deposition (PECVD) has desirable properties such as good adhesion, low pinhole density and good step coverage [Kim et al., 1998; Takadom et al., 2003]. Most of the carbon nitride films prepared are amorphous, having far lower N/C ratios than the stoichiometric value of C₃N₄. To date no one has reported the formation of nanodots and nanostripes of the PECVD-grown amorphous carbon nitride (a-CN) utilizing a plasma and thermal treatment technique. The well aligned or arranged nanostructures of a-CN could be useful for a precise control of liquid-crystal arrangement.

In this work, we grew the carbon nitride films on Si(100) by PECVD at room temperature, followed by surface treatments with H₂ plasma and thermal annealing. Such a procedure resulted in the formation of nanodots and nanostripes of a-CN. We discuss the results in terms of chemical composition, bonding structure, surface morphology, and optical properties of the nanostructures.

EXPERIMENTAL

†To whom correspondence should be addressed.
E-mail: ybhahn@chonbuk.ac.kr

Amorphous carbon nitride films were deposited on Si(100) at room temperature (RT) in a PECVD (13.56 MHz) reactor using CH₄ and N₂. The Si(100) substrate was dipped in BOE (NH₄F : HF = 6 : 1) solution followed by ultrasonic cleaning in acetone and methanol before the substrate was loaded. The base pressure of reactor was kept at to 1×10^{-3} Torr, and the working pressure was 3 Torr. Before growing the a-CN films, the substrate was treated with H₂ plasma at 40 W RF power and 500 °C for 10 min. The source gases were then introduced into the reactor through the upper electrode and their flow rates were controlled by mass flow controllers (MFCs). The carbon nitride films were quite dependent of temperature, growth time, and RF power. Unless mentioned, the a-CN films were grown at room temperature and 60 W for 60 min. To form nanostructures, the as-deposited a-CN films having thickness of about 400 nm were treated by H₂ plasma for 10 min at RT and followed by thermal annealing in nitrogen atmosphere at 200 and 300 °C for 10, 20, and 30 min.

Chemical bonding structure and elemental depth profile of the nanostructures were observed by Fourier transform infrared spectroscopy (FT-IR) and Auger electron spectrometry (AES), respectively. The samples were also characterized by atomic force microscope (AFM) with tapping mode and photoluminescence (PL) measurements for structural and optical properties, respectively.

RESULTS AND DISCUSSION

Fig. 1 shows AFM images of as-grown and plasma-treated a-CN films on Si (100). The a-CN film grown by PECVD at RT showed a smooth surface morphology (rms=0.65 nm), but the plasma-treated by H₂ discharges showed a rough surface (rms=4.376 nm) mainly because of sputtering and/or etching effect, a typical result in the case of H₂-plasma treatment of thin films. It is interesting that a high density of nanosized dots is formed by the plasma treatment. The plasma-treated films were followed by annealing at 300 °C for different times. The as-grown and the annealed samples were also subject to AES analysis and AFM observations. Although not illustrated, the AES depth profiles showed a uniform concentration distribution throughout the a-CN film with composition of 90% C and 10% N.

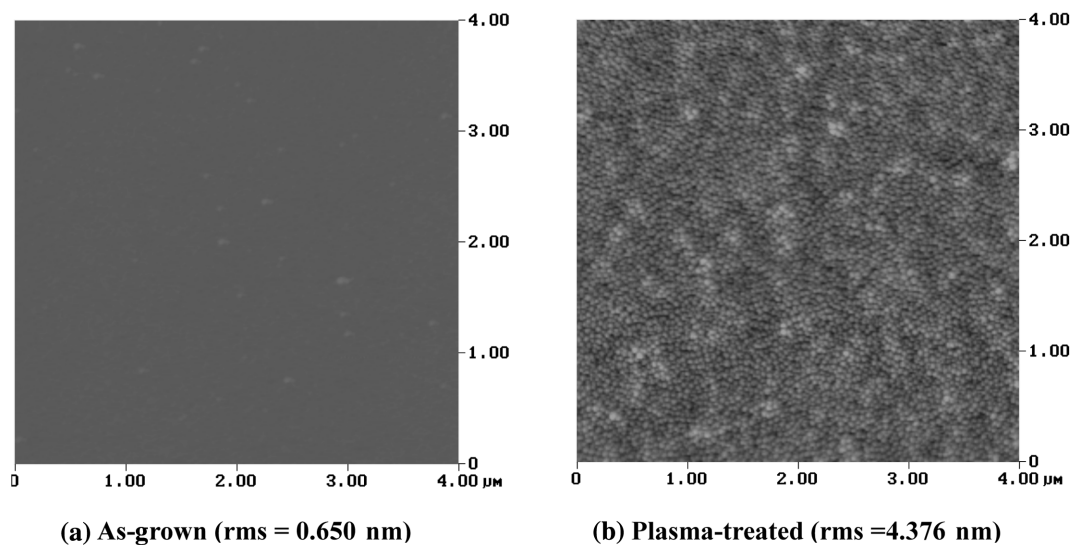


Fig. 1. AFM images of as-grown and plasma-treated a-CN films.

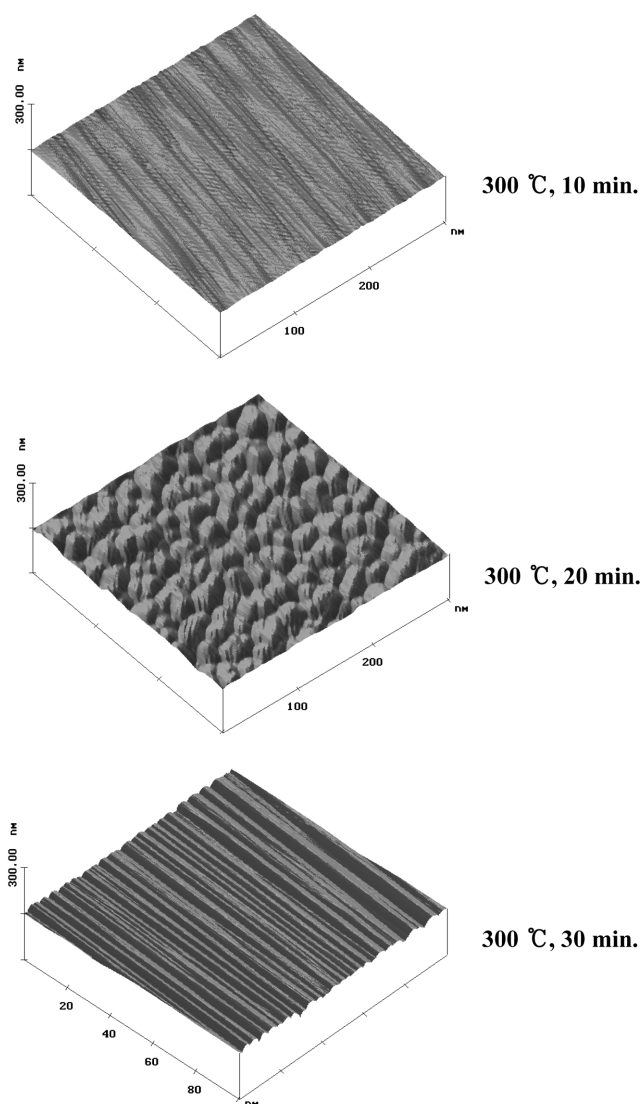


Fig. 2. AFM images showing the morphological evolution of a-CN by annealing at 300 °C for different times.

March, 2006

Fig. 2 shows the AFM images obtained from the annealed samples at 300 °C for 10, 20, and 30 min. They present the morphological evolution of a-CN from thin film to nanostructures. Densely and uniformly distributed nanodots (~25 nm diameter and ~30 nm height) and nanostripes (~5 nm width and ~20 nm height) were formed after 20 and 30 min. annealing, respectively. These results indicate that the dimension and configuration of the a-CN nanostructures are to be controlled by a precise control of the thermal history of the plasma-treated films. The formation of nanodots (i.e., 3D coherently strained islands) is probably attributed to the formation of islands and clusters. A high density of small dots generated during the H₂-plasma treatment migrates and forms clusters up to a size with the aid of thermal annealing. When more adatoms encounter critical-sized clusters they form stable clusters, resulting in formation of nanodot-like structures. By contrast, the nanostripes (i.e., periodically faceted structures) could be described as equilibrium structures, which are observed upon thermal annealing or upon interruption of crystal growth [Shchukin et al., 1999]. In such a case, intrinsic surface energy is a driving force for the periodic ordering of the nanostructures. However, to clearly understand the formation mechanism of the a-CN nanostructures, further study is required in terms of thermodynamics and/or kinetics theory.

Fig. 3 shows the FT-IR spectra for the as-grown films and the annealed samples at 300 °C for different times. The as-grown a-CN film presents various bonding peaks: C-N at 900-1,200 cm⁻¹, C=C stretching mode at 1,300-1,500 cm⁻¹, C=N at 1,640-1,670 cm⁻¹, CH_n bending at 1,350-1,400 cm⁻¹, CH_n stretching band at 2,700-2,900 cm⁻¹, and N-H stretching mode at 3,200-3,500 cm⁻¹. The annealing treatment induced a film structure change. The IR spectra of annealed samples show three dominant peaks: the overlap of C=N and C=C stretching modes at 1,500-1,800 cm⁻¹, C≡N stretching vibration at 2,100-2,250 cm⁻¹, CH_n stretching vibration at 2,700-2,900 cm⁻¹, and N-H stretching band at 3,200-3,500 cm⁻¹. It is worthwhile to note that the peak intensity of the C≡N bond somewhat increased with annealing time.

The optical properties of a-CN films were examined by PL measurements because of their possible applications in optical devices.

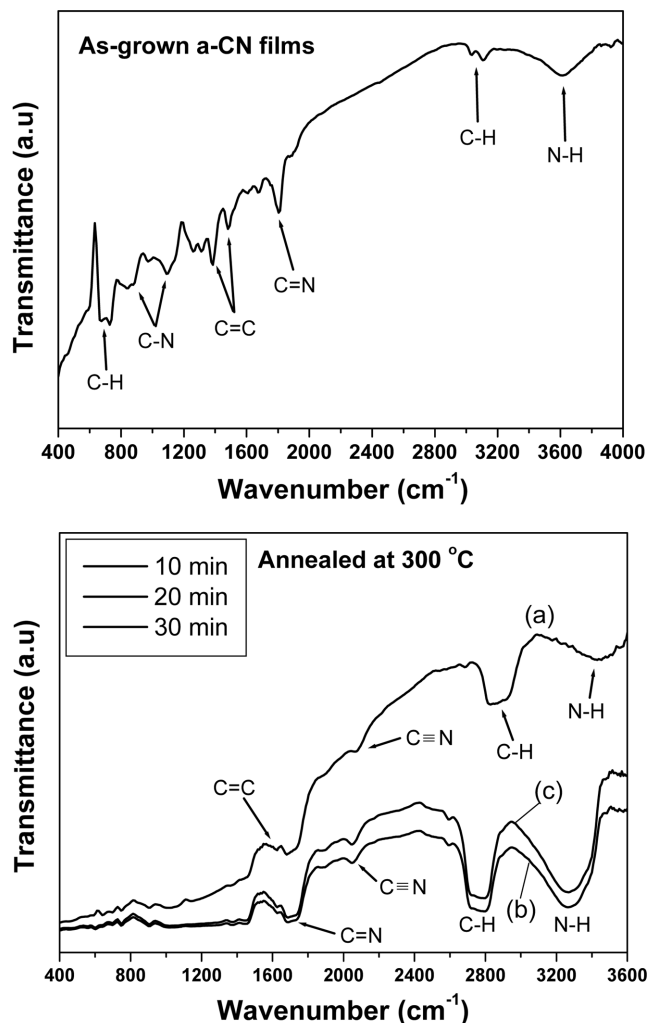


Fig. 3. FT-IR spectra of the as-grown (top) and annealed a-CN at 300 °C for (a) 10, (b) 20, and (c) 30 min (bottom).

Fig. 4 shows the room temperature PL spectra obtained from the as-grown and the a-CN annealed at 300 °C, the same samples as used in Fig. 2. The PL spectra of annealed samples show somewhat different from the as-grown a-CN film: the former exhibits a strong emission peak at 2.2 eV, but the latter contains two emission peaks at about 2.1 and 2.4 eV. It is also interesting to see that the nanostructures show a stronger peak intensity than the as-grown a-CN film. This could be attributed to a quantum effect resulting from a structure change caused by the annealing treatment as shown in Fig. 2. Several research groups have observed PL property from a-CN films and related it to that of a-C:H films where the origin of the PL might be attributed to a recombination of confined electron-hole pairs in sp^2 clusters [Mutsukura, 2001; Mutsukura and Akita, 1999; Hayashi et al., 2001; Klyui et al., 1998; Robertson, 1996; Rusli and Robertson, 1996; Heitz et al., 1999]. However, up to now, the PL mechanism of the a-CN nanostructures has not been well understood and requires a further study.

SUMMARY AND CONCLUSION

Nanodots and nanostripes of a-CN on Si(100) were formed by

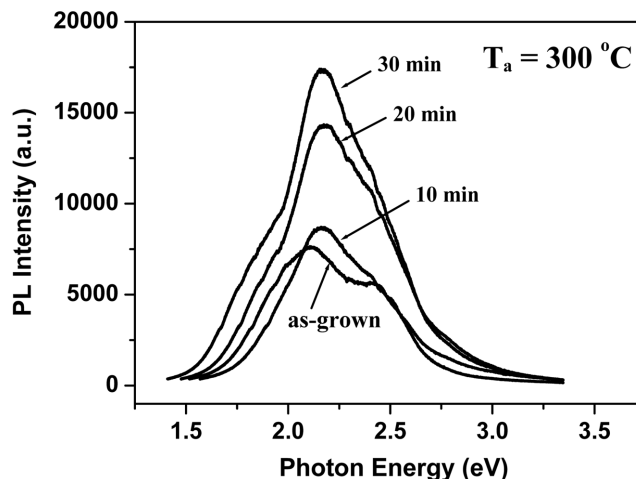


Fig. 4. Room temperature PL spectra obtained from the as-grown and the annealed a-CN at 300 °C for 10, 20, and 30 min.

treating the PECVD-grown films with H_2 plasmas and thermal annealing. The dimension and configuration of the a-CN nanostructures were affected by annealing temperature and treatment time. The IR spectra of annealed samples showed three dominant peaks: the overlap of C=N and C=C stretching modes at 1,500-1,800 cm^{-1} , C≡N stretching vibration at 2,100-2,250 cm^{-1} , CH_n stretching vibration at 2,700-2,900 cm^{-1} , and N-H stretching band at 3,200-3,500 cm^{-1} . The as-grown a-CN films exhibited two emission peaks at 2.1 and 2.4 eV, but the annealed a-CN nanostructures showed a strong one emission peak at 2.2 eV.

ACKNOWLEDGMENT

This paper was supported by the Brain Korea 21 Project in 2005.

REREFENCES

- Hayashi, Y., Krishna, K. M., Ebisu, H., Soga, T., Umeno, M. and Jimbo, T., "Optical and structural properties of nitrogen doped amorphous carbon films grown by rf plasma-enhanced CVD," *Diamond and Related Materials*, **10**, 1002 (2001).
- Heitz, T., Godet, C., Bouree, J. E., Drevillon, B. and Conde, J. P., "Radiative and nonradiative recombination in polymerlike α -C:H films," *Phys. Rev. B*, **60**, 6045 (1999).
- Inoue, T., Ohshio, S., Saitoh, H. and Kamata, K., "Preparation of nitrogen containing carbon films using chemical vapor deposition enhanced by electron cyclotron resonance plasma," *Appl. Phys. Lett.*, **67**, 353 (1995).
- Ju, J., Xia, Y., Zhang, W., Wang, L. and Tang, D., "Infrared optical properties of amorphous hydrogenated carbon nitride film," *J. Non-Crystalline Solids*, **278**, 213 (2001).
- Kim, J. W., Kim, D. O. and Hahn, Y. B., "Effect of rapid thermal annealing on the structural and electrical properties of TiO_2 thin films prepared by plasma enhanced CVD," *Korean J. Chem. Eng.*, **15**, 217 (1998).
- Kim, S. H., Umar, A. and Hahn, Y. B., "Growth and formation mechanism of sea urchin-like ZnO nanostructures on Si," *Korean J. Chem. Eng.*, **22**, 489 (2005).

- Kim, T. Y., Lee, S. H., Mo, Y. H., Nahm, K. S., Kim, J. Y., Suh, E. K. and Kim, M., "Growth mechanism of needle-shaped ZnO nanostructures over NiO-coated Si substrates," *Korean J. Chem. Eng.*, **21**, 733 (2004).
- Kundoo, S., Chattopadhyay, K. K., Banerjee, A. N. and Nandy, S. K., "Synthesis and optical characterization of amorphous carbon nitride thin films by hot filament assisted RF plasma CVD," *Vacuum*, **69**, 495 (2003).
- Lim, S. F., Wee, A. T. S., Lin, J., Chua, D. H. C. and Huan, C. H. A., "On the nature of carbon nitride nanocrystals formed by plasma enhanced chemical vapor deposition and rapid thermal annealing," *Chem. Phys. Lett.*, **306**, 53 (1999).
- Lou, H. Q., Axen, N., Somekh, R. E. and Hutchings, I. M., "Mechanical properties of amorphous carbon nitride films," *Diamond and Related Materials*, **5**, 1303 (1996).
- Muhl, S. and Mendez, J. M., "A review of the preparation of carbon nitride films," *Diamond and Related Materials*, **8**, 1809 (1999).
- Mutsukura, N., "Photoluminescence and infra-red absorption of annealed a-CN_x:H films," *Diamond and Related Materials*, **10**, 1152 (2001).
- Mutsukura, N. and Akita, K.-I., "Deposition of hydrogenated amorphous CN_x film in CH₄/N₂ RF discharge," *Diamond and Related Materials*, **8**, 1720 (1999).
- Klyui, N. I., Piryatinskii, Yu. P. and Semenovich, V. A., "Intensive visible photoluminescence of a-C:H:N films," *Materials Letters*, **35**, 334 (1998).
- Robertson, J., "Recombination and photoluminescence mechanism in hydrogenated amorphous carbon," *Phys. Rev. B*, **53**, 16302 (1996).
- Rusli, Amaratunga G. A. and Robertson, J., "Polarization memory of photoluminescence in amorphous carbon," *Phys. Rev. B*, **53**, 16306 (1996).
- Shchukin, Vitaliy A. and Bimberg, D., "Spontaneous ordering of nanostructures on crystal surfaces," *Rev. Mod. Phys.*, **71**, 1125 (1999).
- Takadom, J., Rauch, J. Y., Cattenot, J. M. and Martin, N., "Comparative study of mechanical and tribological properties of CN_x and DLC films deposited by PECVD technique," *Surface and Coating Technology*, **174-175**, 427 (2003).
- Wang, J., de Moraes, M. A. B., Barabauskas, V. and Durrant, S. F., "Hydrogen-containing carbon nitride films produced by the combined hot filament-plasma CVD technique," *Thin Solid Films*, **377-378**, 280 (2000).
- Wei, J., "Formation of β -C₃N₄ crystals at low temperature," *J. Appl. Phys.*, **89**, 4099 (2001).
- Yu, G.-Q., Lee, S.-H. and Lee, J.-J., "Effects of thermal annealing on amorphous carbon nitride films by r.f. PECVD," *Diamond and Related Materials*, **11**, 1633 (2002).
- Xu, W., Fujimoto, T., Li, B. and Kojima, I., "Characterization of the density, structure and chemical states of carbon nitride films," *Appl. Sur. Sci.*, **175-176**, 456 (2001).