



PHOTOSENSITIVITY OF GRAPHITIC CARBON NITRIDE FILMS OBTAINED BY EVAPORATION

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Abstract: Graphitic carbon nitride (g-C₃N₄) comprises a two-dimensional sheet of carbon and nitrogen atoms. In the present study, g-C₃N₄ films were prepared by evaporating guanidine carbonate for evaluating the photosensitivity of the films. The X-ray diffraction peak of the g-C₃N₄ films was observed at $2\theta=27.6^\circ$, corresponding to interlayer stacking. The N/C atomic ratio obtained by energy dispersive X-ray spectroscopy was approximately 133%. The results indicated characteristics associated with two-dimensional carbon and nitrogen atom structures. The optical energy gap was estimated to be 2.88 eV at N/C =136%, and it decreased with elevation in substrate temperature. Photo sensitivity spectra were obtained by irradiation with monochromatic light. The photocurrent originated from electronic transition between energy bands because the photon energy at which the photo sensitivity increases was consistent with the optical energy gap.

Keywords: Graphitic carbon nitride; photosensitivity; photocurrent; optical absorption spectra

INTRODUCTION

Carbon compounds are used to produce multiple organic compounds including hydrocarbons and inorganic compounds such as CO₂ and SiC. The crystalline formation of carbon nitride is more difficult than that of silicon nitride. Ever since Lie and Cohen reported that carbon nitride can show stability via theoretical calculations [1], many groups have attempted to prepare crystalline C₃N₄ using chemical vapor deposition, sputtering, and arc ion plating [2-10]. Samples obtained in their studies were usually amorphous carbon nitride (a-CN_x) because nitrogen is difficult to incorporate into a carbon network. Furthermore, carbon nitride can exist with polymeric formations. The synthesis method of crystalline C₃N₄, such as α -C₃N₄ or β -C₃N₄, has not been established.

Berzelius et al. (1834) reported the synthesis of a polymeric carbon nitride for the first time [11]. Presently, polymeric carbon nitride is called graphitic carbon nitride (g-C₃N₄) because it comprises a two-dimensional sheet such as graphite. g-C₃N₄ is easily synthesized by thermal polymerization of melamine and dicyandiamide [12]. g-C₃N₄ powder is a semiconductor with an energy band gap of 2.7 eV; furthermore, it shows photo catalytic properties of organic contaminant degradation. Although the photo catalytic efficiency of pure g-C₃N₄ is very less, the addition of a small amount of Pt nano particles activates H₂ production [13]. After this discovery, compared to titanium dioxide (TiO₂), g-C₃N₄ has been actively studied as a new photo catalyst. Thus, g-C₃N₄ can possibly be applied to the material in an environmental improvement system for organic pollution in air [14]. However, g-C₃N₄ has not been quantitatively evaluated because g-C₃N₄ is obtained in the powdered form when melamine is used for the synthesis. In this study,

the structure and optical properties of g-C₃N₄ films prepared by guanidine carbonate evaporation are discussed.

EXPERIMENTAL

g-C₃N₄ Film Preparation

The g-C₃N₄ films were prepared using an evaporation method reported by Miyajima (2014) [15]. Guanidine carbonate (97% pure) was used as the source material. Guanidine carbonate (3.0 g) was placed at the bottom of the quartz test tube, as shown in Figure 1. Borosilicate glass or quartz substrates were also placed in the tube away from the guanidine carbonate. The tube was capped with quartz wool. It was heated in air to a target temperature of 600°C–630°C at a rate of 10 °C/min using a tube furnace (NISSIN SEIKI CO., LTD, TMF-300N). The temperature was kept constant for 2 h. After heating, the tube was naturally cooled to room temperature. The heating caused the polymerization of guanidine carbonate and the polymer was subsequently evaporated [15]. The evaporated polymer formed g-C₃N₄ sheets on the substrate.

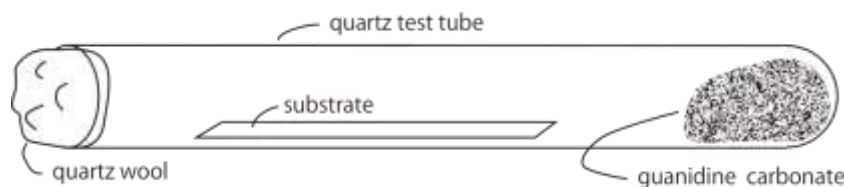


Figure 1. Apparatus for preparing g-CN_x films using guanidine carbonate.

Energy Dispersive X-Ray Spectroscopy and X-Ray Diffraction

A scanning electron microscope (SEM, Hitachi HighTechnologies, S-3400N) was used to observe the film's surface. The elemental composition of g-C₃N₄ films was estimated using energy dispersive X-ray spectroscopy (EDS, Horiba, X-MAX50). X-ray diffraction (XRD, Rigaku SmartLab) was used to determine the crystalline structure of films. The wavelength of the X-ray beam was $\lambda = 1.54 \text{ \AA}$ (Cu K α).

Optical Energy Gap

The optical transmittance spectra were obtained using a UV-VIS-NIR spectrometer (Shimadzu, UV-3150). The thickness and refractive index were calculated using spectral oscillation of optical interference. The optical energy gap E_{04} was defined as the photon energy at which the optical absorption coefficient was 10^4 cm^{-1} .

Photosensitivity

For electrical measurements, gap electrodes of aluminum were created on the sample

surfaces using a vacuum evaporation method. The gap and width of the electrodes were 60 μm and 5 mm, respectively. Samples were illuminated by monochromatic light passed through a monochromator and optical filters using a Xe lamp as a light source. The current was monitored by applying a constant voltage of 20 V to electrodes using a source meter (Keithley 2635B). The photocurrent was defined as the difference between the dark and illuminated currents. Normalization of photocurrent is usually required because the incident light power varies by the wavelength of the monochromatic light. We used spectroscopic photosensitivity (A/W), defined as photocurrent divided by incident light power into the surface area between electrodes, for normalization.

RESULTS AND DISCUSSION

Structural analysis

Figure 2 shows the atomic concentration of a $g\text{-C}_3\text{N}_4$ film obtained by EDX. The concentrations of silicon, aluminum, and oxygen increased with increasing electron accelerating voltage. The detected presence of these atoms was due to signals from the sample substrate. Therefore, the atomic concentration represents accurate values at lower electron accelerating voltage. In this study, the N/C ratio was determined using the concentration at an electron accelerating voltage of 3 kV. Figure 3 shows the N/C atomic ratio and the thickness of $g\text{-C}_3\text{N}_4$ films as a function of distance D from the edge of guanidine carbonate powder. The film was thickest at $D=65$ mm. The N/C ratios were almost flat and approximately 1.33, which were agreeable with that of $g\text{-C}_3\text{N}_4$ powder having the theoretical structure of a CN network sheet.

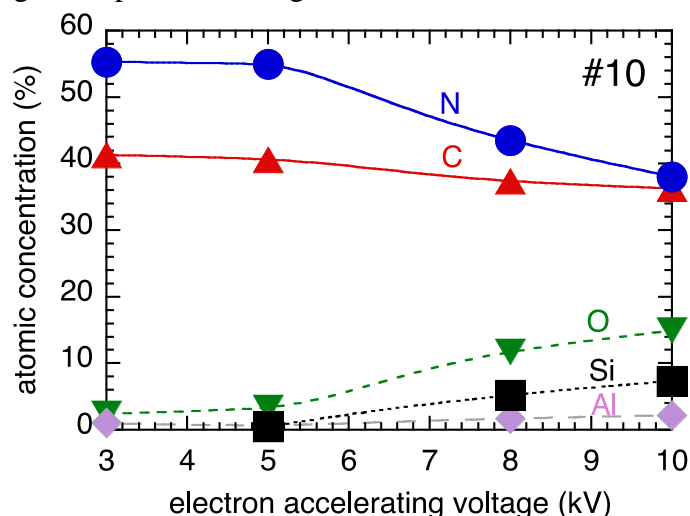


Figure 2. The atomic concentration of a $g\text{-C}_3\text{N}_4$ film as a function of electron accelerating voltage.

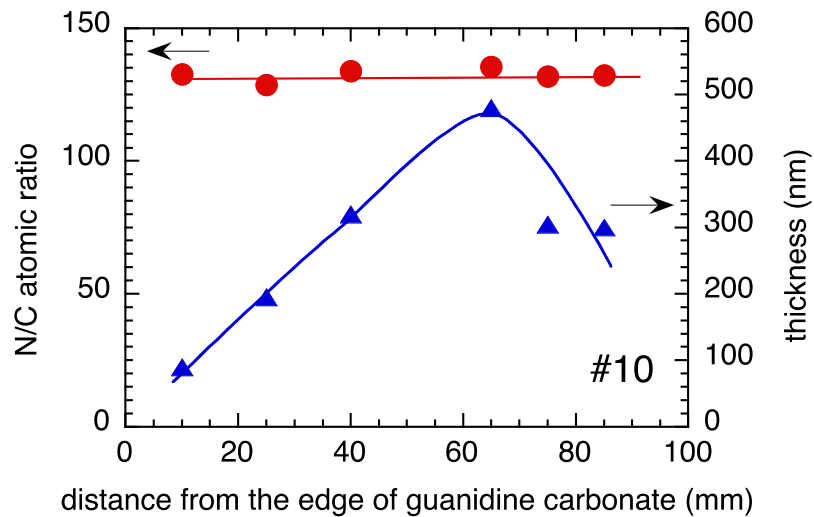


Figure 3. The N/C atomic ratio and the thickness of g-C₃N₄ films as a function of the distance from the edge of guanidine carbonate, where they are represented by circle and triangle plots, respectively.

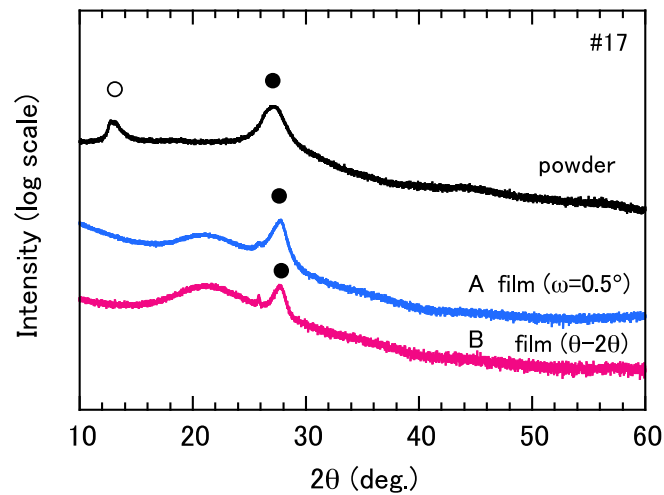


Figure 4. XRD pattern of g-C₃N₄ powder and film, where lines A and B were obtained by $q - 2q$ and the grazing angle method, respectively.

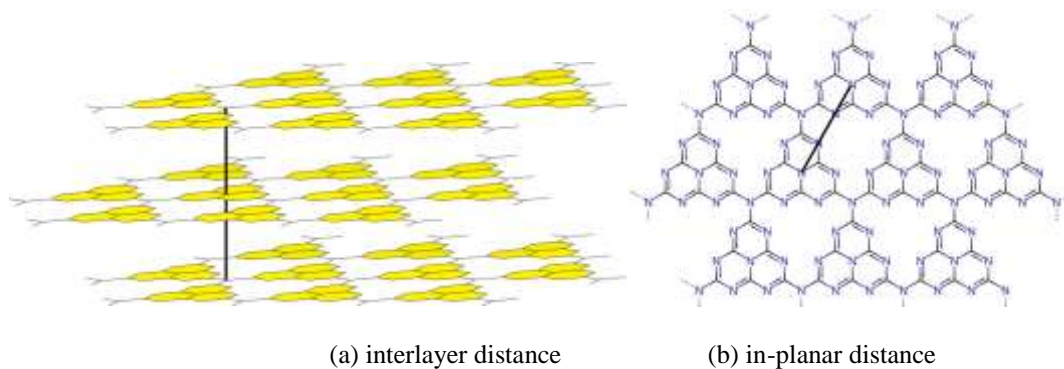


Figure 5. Structure of g-C₃N₄ and the distance between diffraction planes.

Figure 4 shows XRD patterns of the remaining powder after heating and a g-C₃N₄ film. As for XRD measurement of the film, two methods were used. One was the $q-2q$ method and the other was the grazing angle method, where the incident angle ω was fixed at 0.5° . The XRD pattern of the powder was owing to a typical g-C₃N₄ structure [13]. The main peak indicated by a solid circle ($2\theta=27.6^\circ$) corresponded to interlayer stacking as shown in Figure 5 (a). The peak indicated by an open circle ($2\theta=12.8^\circ$) originated from an in-planar repeat period, such as the distance between pores as shown in Figure 5(b). This peak did not appear on the XRD pattern of the film. This could be because the sheet size of the CN network of the film is smaller than that of g-C₃N₄ powder. The appearance of the main peak with the grazing angle method indicates that the g-C₃N₄ sheet was not aligned in the direction parallel to the substrate.

Optical Properties

The temperature at the center of the furnace was different from the substrate temperature because of uneven temperature distribution in the furnace. Therefore, g-C₃N₄ films were prepared while monitoring the substrate's temperature T_s during heating. Figure 6 shows the N/C ratio and optical energy gap E_{04} with various T_s . Note that E_{04} decreased with elevating T_s . Heating at high temperature was needed to obtain an energy gap less than 3.0 eV (energy gap of rutile titanium dioxide) for the g-C₃N₄ film. When the heating temperature was low, thermal polymerization was not very active. Therefore, the N/C ratio of the film at lower T_s was approximately close to that of the precursor. In this case, the N/C ratio theoretically increased with decreasing T_s because melem (C₆N₇(NH₂)₃) was the precursor of g-C₃N₄. The experimental results differed from our hypothesis; however, the reason for this is currently unknown.

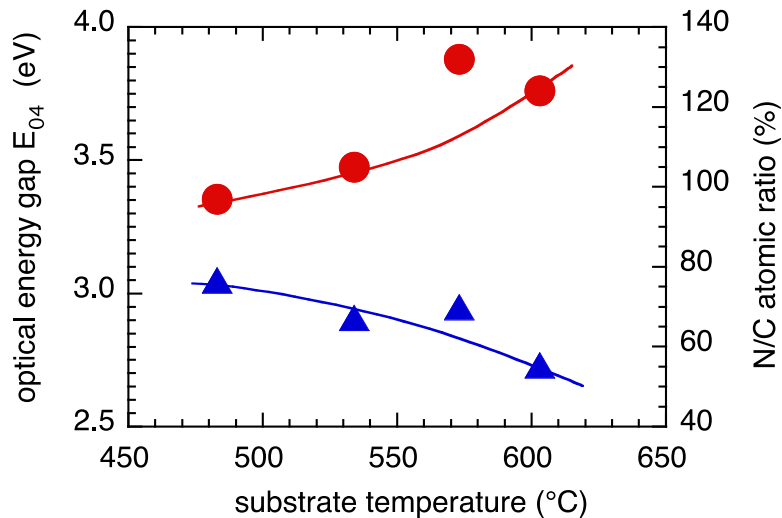


Figure 6. The optical energy gap E_{04} and N/C atomic ratio with various substrate temperatures.

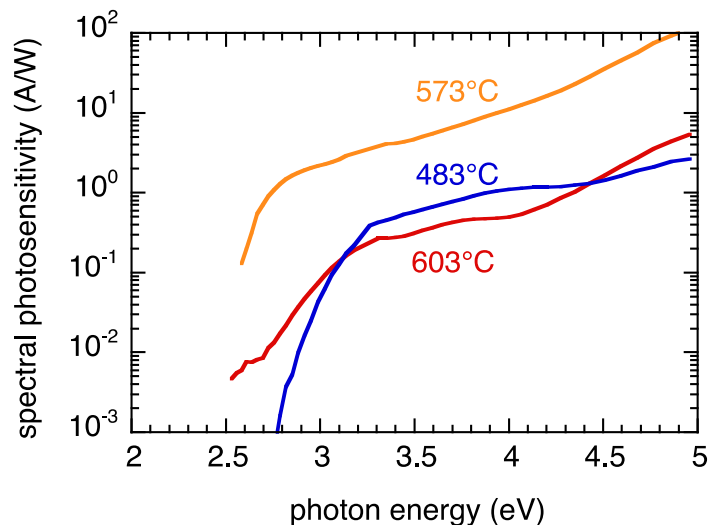


Figure 7. The spectral photosensitivity of g-C₃N₄ films with various substrate temperatures.

Figure 7 shows spectral photosensitivity of g-C₃N₄ films with various T_s . The magnitude of photosensitivity was different among samples because of differences in film thickness and surface conditions. The photosensitivity spectrum of the film at $T_s=483^\circ\text{C}$ and 573°C showed increases of approximately 3.0 and approximately 2.6 eV, respectively. The edge of photosensitivity of the film at $T_s=603^\circ\text{C}$ was obscure. This could be because the photocurrent originated from electronic transition between energy bands because the photon energy at which the photosensitivity rose was consistent with the optical energy gap.



CONCLUSIONS

In our study, the g-C₃N₄ films were prepared via evaporation of guanidine carbonate to evaluate their photosensitivity. The N/C atomic ratio was approximately 133%. The diffraction caused by the CN network layer was observed by XRD; however, an in-planar repeat period, such as the distance between pores of nitrogen, was not confirmed. We estimated that the CN sheet size of films was smaller than that of original g-C₃N₄ powder. The optical energy gap E₀₄ was estimated to be 2.88 eV at N/C = 136%. This value is smaller than the energy gap of rutile titanium dioxide. Moreover, the photocurrent of g-C₃N₄ films was observed. We confirmed that the photocurrent flows because of electronic transition between energy bands. Therefore, the application of g-C₃N₄ as a photo catalytic material is advantageous for efficient conversion of solar light.

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