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Optical properties of graphitic carbon nitride films prepared by evaporation

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ABSTRACT

Graphitic carbon nitride (g-C_3N_4) consists of two-dimensional sheets of carbon and nitrogen atoms. Films of g-C_3N_4 were prepared by evaporating guanidine carbonate at four different substrate temperatures. The optical absorption band of the films appears at 3.3 eV and the optical energy gaps are calculated to be 2.83–2.90 eV. Band intensity increases with increasing substrate temperature, but the energetic band position does not shift. The photocurrent of g-C_3N_4 films can be observed by irradiation with monochromatic light. While the photosensitivity spectra are in almost complete correspondence with the optical absorption spectra, it is also found that the photocurrent is generated by irradiation at photon energies below the optical energy gap down to 2.5 eV.

1. Introduction

Liu and Cohen reported that carbon nitride (C_3N_4) can show stability via theoretical calculations [1]. They showed that C_3N_4 can have bulk modulus comparable to or greater than that of diamond with theoretical calculations. However, it is difficult to synthesize three-dimensional crystalline C_3N_4 such as α-C_3N_4 and β-C_3N_4 because carbon nitride synthesized by chemical or physical vapor deposition is almost amorphous [2,3]. Although rhombohedral phase carbon nitride (r-C_3N_4), which consists of two-dimensional (2D) sheets and a stacking structure, did not show high bulk modulus in their work, the synthesis has already been demonstrated by Liebig and Berzelius [4]. Presently, r-C_3N_4 is also known as graphitic carbon nitride (g-C_3N_4) [5]. Graphitic carbon nitride is a semiconductor with a band gap around 2.7 eV and has been found to exhibit photocatalytic properties for organic contaminant degradation [6]. While the photocatalytic efficiency of pure g-C_3N_4 is considerably small, adding a small amount of Pt nanoparticles activates H_2 production. Similar to the evolution of the field of TiO_2 photocatalysts, following this discovery, g-C_3N_4 has been actively studied as a basis for the development of new photocatalysts [7]. It is also expected that g-C_3N_4 will be used as a semiconductor material in electronic device applications.

The use of g-C_3N_4-based materials in electronics is hindered by the current limitation of g-C_3N_4 synthesis to the powder form of the material. While g-C_3N_4 powder is easily synthesized by thermal polymerization of melamine, a g-C_3N_4 film with a flat surface cannot be prepared from the g-C_3N_4 powder by a wet process due to the insolubility of the powdered g-C_3N_4. Therefore, new synthesis techniques must be developed for the fabrication of g-C_3N_4 films to develop g-C_3N_4–based optoelectronic materials. The synthesis of planar films will also enable quantitative evaluation of optical properties. Recently, Riken reported a g-C_3N_4 film synthesis by evaporation with guanidine carbonate as a source [8]. In this study, optical absorption spectra of the g-C_3N_4 films prepared following the procedure described in [8] were obtained using photothermal deflection spectroscopy (PDS), and the optical absorption coefficients of g-C_3N_4 were precisely determined for the first time. The photocurrent of the g-C_3N_4 films was obtained by irradiating with monochromatic light.

2. Materials and methods

2.1. Preparation of g-C_3N_4 films

Fig. 1 shows the experimental apparatus for preparation of g-C_3N_4 films. Guanidine carbonate powder with a purity of 97% was placed at the bottom of a quartz test tube. Quartz glass substrates were placed in the tube, 4–10 cm away from the edge of guanidine carbonate powder. The tube was capped with quartz wool and was heated for 2 h in air using a tube furnace (Nissin Seiki Co., Ltd., TMF-300N). It is assumed that the heating causes the polymerization of guanidine carbonate followed by the evaporation of the polymer. The evaporated polymer then forms C_3N_4 sheets on the substrate. Annealing temperatures T_A were set at 600 and 630 °C and a heating rate of 10 °C/min was used. The temperature in the center of the furnace was different from the substrate temperature because of the inhomogeneous temperature distribution in the furnace. Therefore, the substrate temperature T_s was also monitored during heating. T_s is considered an important parameter rather than T_A because melemium ion, which is a precursor of g-C_3N_4,

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