

Preparation of a novel target material for carbon nitride film deposition

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Abstract

To increase the nitrogen content and the degree of crystallinity in carbon nitride films by film deposition techniques (i.e. sputtering, laser ablation etc.), a novel target material composed of carbon nitride has been prepared by UV photo-assisted synthesis. The intention is to replace the traditional graphite target with this material. This synthesis involves photo-chemical reaction of sodium amide and chloroform as carbon and nitrogen sources, respectively, followed by high temperature sintering under flowing nitrogen. Elemental analyses indicate the presence of C, N and H in the target material with a nitrogen to carbon ratio of 0.23. Infrared spectroscopy shows a mixture of sp³ and sp² carbon and sp² nitrogen in the sintered powder. Six diffraction peaks attributable to α -C₃N₄ were observed in XRD pattern. Grains of ~0.3 μ m in diameter in an extended network were also observed in the SEM micrographs. The sintered carbon nitride powder is stable up to 800°C. © 1997 Elsevier Science S.A.

Keywords: Carbon nitride; UV photo-assisted synthesis

1. Introduction

Carbon nitride (C₃N₄) has attracted intensive research since Liu and Cohen [1] predicted the possible existence of a new superhard compound with a bulk modulus comparable to that of diamond. In addition to the high hardness, this new material is expected to possess superior compressive strength, refractive index, thermal conductivity and chemical inertness [2]. Hence, carbon nitride is important from both fundamental and engineering points of view.

Over the past few years, many efforts to prepare C₃N₄ thin films have focused on various processes such as laser ablation [3], RF sputtering [4,5], DC magnetron sputtering [6], ion beam deposition [7], ion implantation [8], ion plating [9], and plasma-enhanced chemical vapor deposition [10]. Most experimental results show the formation of amorphous carbon nitride films with nitrogen content lower than predicted.

Using UV photo-assisted synthesis, we succeeded in making a new material with carbon-nitrogen bonding and a structure similar to α -C₃N₄. This can be used to replace the traditional graphite target. This novel target is expected to be beneficial for film deposition processes by enhancing the

nitrogen content and degree of crystallinity in carbon nitride films.

2. Experimental details

UV photo-assisted synthesis was used to prepare a carbon nitride target by reacting an alkali-metal amide, such as sodium amide, as a nitrogen source with alkyl chloride, such as chloroform, as a carbon source. A schematic diagram for the apparatus used in the process is shown in Fig. 1. All procedures were performed under a nitrogen atmosphere in a dry box due to the strong air sensitivity of alkali metal amide. A 500-W mercury lamp was used as the UV source to activate the reaction. Upon completion of the reaction, water was then added to decompose the unreacted alkali amide and to remove the by-product of alkali chloride. After a series of pumping and filtration processes, a precursor of chlorine-containing carbon nitride was obtained. A black amorphous powder of carbon nitride was then obtained by baking the precursor with chlorine at 250°C under flowing nitrogen to remove the remaining water and to eliminate the remaining chlorine as HCl. The carbon nitride powder was further sintered at 800°C under nitrogen to enhance the amorphous crystalline transformation.

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Table 1

The results of the elemental analyses for the chlorine-containing carbon nitride precursor

Element	N	C	H
Weight %	11.05	41.25	2.60

Operational condition: combustion to 800°C in oxygen atmosphere.

3. Results and discussions

3.1. Composition and thermal stability

The chemical composition of the chlorine-containing carbon nitride precursor by elemental analysis is shown in Table 1. It is noted that the total content of C, N and H is only 55% due to the fact that chlorine is eliminated from the precursor during heating from 200°C to 300°C by combining with hydrogen to form hydrogen chloride. The detailed thermolysis behavior for this precursor powder is shown in Fig. 2, showing 50% weight loss after heating to 300°C. This is in good agreement with the results shown in Table 1. Note that the mole ratio of N to C for the precursor is about 0.23, which is lower than the theoretical value of 4/3, but is comparable with the reported values for most of the carbon nitride films prepared by high energy plasma pro-

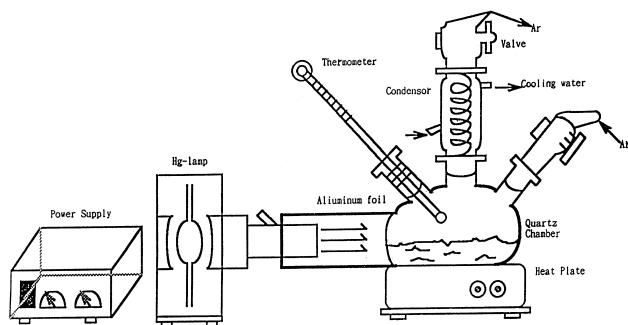


Fig. 1. Schematic diagram for the UV photo-assisted synthesis reaction.

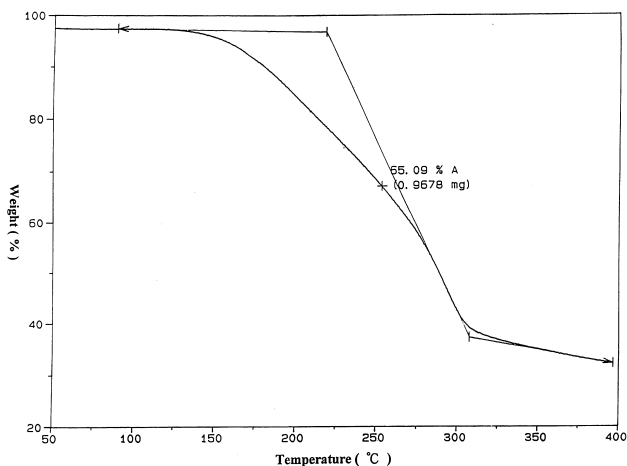


Fig. 2. Typical thermogravimetric analysis diagram for the chlorine-containing carbon nitride precursor.

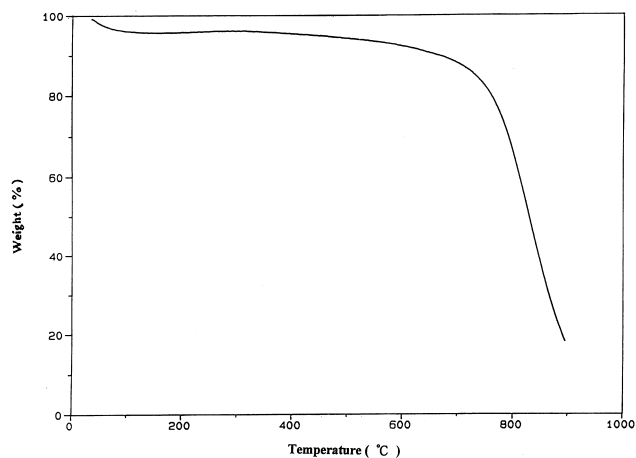


Fig. 3. Typical thermogravimetric analysis diagram for the sintered powders.

cesses. The observation of a low N/C ratio of the precursor or film samples can be rationalized in terms of the electron expelling effects of the nitrogen lone pairs [11]. The sintered carbon nitride powders were characterized by thermogravimetric analysis (TGA), and a typical TGA result is shown in Fig. 3. The weight loss around 100°C is attributed to the removal of absorbed water, and the precursor is stable up to 800°C. It signifies stronger thermal stability of carbon nitride compared with the usual organic compounds containing C–N bonding and suggests an extended C–N covalent network structure within the sample [3].

3.2. Bonding characterizations

A typical IR transmittance spectrum for a sintered carbon nitride sample is shown in Fig. 4. Absorption peaks at 1618 cm^{-1} and 1384 cm^{-1} can be assigned as the vibrational modes of C=N stretching and CH_3 bending, respectively [12]. It indicates that the bonding between C and N consists

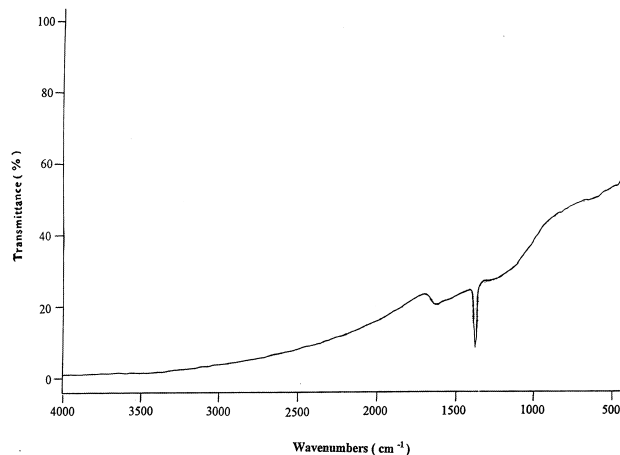


Fig. 4. Typical infrared transmittance spectrum for the packed disk of sintered powders and KBr.

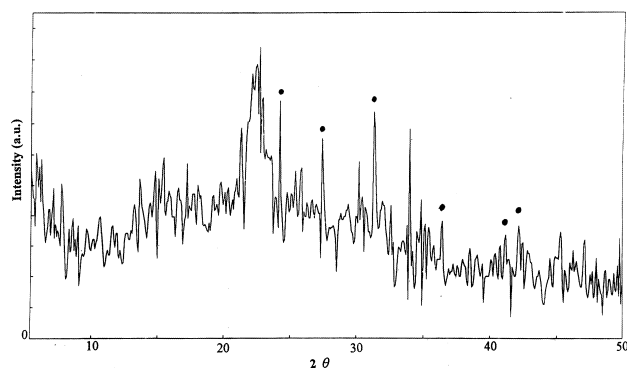


Fig. 5. Typical XRD pattern for the sintered powders.

of sp^3 and sp^2 carbon and sp^2 nitrogen. The C–Cl stretching vibration at 671 cm^{-1} disappeared after the heat treatment under flowing nitrogen gas.

3.3. Crystal structure and morphology

Fig. 5 shows the X-ray diffraction pattern of carbon nitride powders after sintering at 800°C . As shown in Table 2, there are six diffraction peaks at $2\theta = 24.12^\circ$, 27.32° , 31.24° , 36.36° , 41.16° and 42.12° , which correspond to peak positions of the theoretical $\alpha\text{-C}_3\text{N}_4$ diffraction pattern [4] for the following (h,k,l) interplanar spacings: 0.3686 nm (1,0,1), 0.3262 nm (1,1,0), 0.2861 nm (2,0,0), 0.2469 nm (2,0,1), 0.2191 nm (1,0,2) and 0.2143 nm (2,1,0), respectively. This observation is also in good agreement with the theoretical analysis that $\alpha\text{-C}_3\text{N}_4$ is the most stable structure [13]. The broad feature around 23° indicates the presence of an amorphous extended network in the sintered material. Further investigation to improve the crystallinity of the precursor is in progress. The typical morphology of the sintered carbon nitride powder is shown in Fig. 6. The material appears to be granular with average grain size of $0.3\text{ }\mu\text{m}$ in diameter.

Table 2

Comparison of XRD data of the powders with the calculated powder pattern of $\alpha\text{-C}_3\text{N}_4$

XRD		Calculated $\alpha\text{-C}_3\text{N}_4$ pattern		
d (nm)	Normalized intensity ratio (%)	d (nm)	$h k l$	Intensity ^a
		0.5664	1 0 0	w
0.3686	100	0.3635	1 0 1	s
0.3262	85	0.3270	1 1 0	m
0.2861	95	0.2832	2 0 0	m
0.2469	51	0.2431	2 0 1	s
		0.2370	0 0 2	w
0.2191	46	0.2186	1 0 2	m
0.2143	54	0.2141	2 1 0	s

2θ from 5° to 50° .

^aDiffraction intensities: s, strong; m, medium; w, weak.

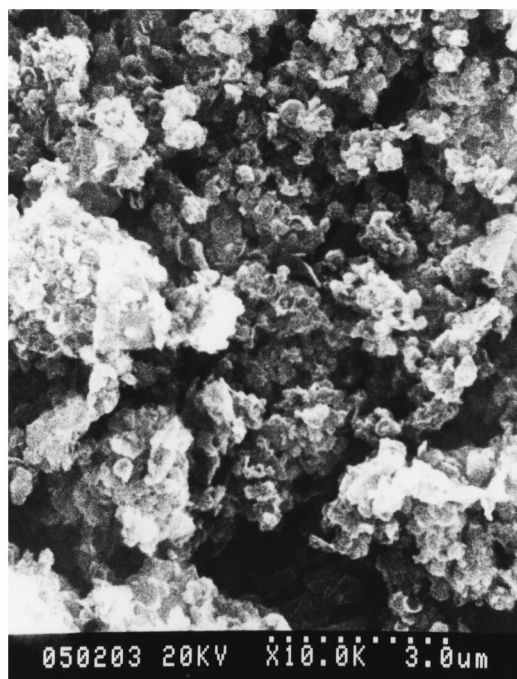


Fig. 6. Typical SEM micrograph showing morphology of the sintered powder.

4. Conclusions

Crystalline carbon nitride was prepared successfully by a photo-assisted synthetic process using sodium amides and chloroform as the nitrogen and carbon sources, respectively. Our results indicate that the carbon nitride obtained by heat treatment of the precursor crystallizes as $\alpha\text{-C}_3\text{N}_4$ structure with a nitrogen to carbon ratio of 0.23. This carbon nitride powder is stable up to 800°C . When used as a target for future film deposition, this new material is expected to be beneficial to increase the nitrogen content and degree of crystallinity in carbon nitride films.

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