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Optimization of reaction parameters for synthesis of amorphous silicon nitride powder by vapor phase reaction

Yong Kwon Chung[a,b], Jae Hong Koo[a], Shin A. Kim[a], Eun Ok Chi[a], Jee Hyun Hahn[a], Chan Park[b,c,*]

[a]Research and Development Center, OCI company Ltd., Seongnam 462-120, Republic of Korea
[b]Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Republic of Korea
[c]Research Institute of Advanced Materials, Seoul National University, Seoul 151-744, Republic of Korea

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Abstract

Most silicon nitride powders, which are industrially used in various applications under extreme conditions, are produced by the diimide process. The synthesis of diimide is carried out at −50–0 °C using liquid-phase reactants with organic solvent. This process, however, consumes a considerable amount of energy. One promising method for the synthesis of silicon nitride powder which is also energy-efficient is the vapor-phase reaction of $SiCl_4$ with NH_3. In this study, the processing parameters of the vapor-phase reaction for the synthesis of silicon nitride were investigated to use this method for producing diimide. The vapor-phase reaction was completed at room temperature with a down-top flow, and solid products were obtained at the bottom of the reactor. $Si(NH)_2$ was decomposed at temperatures above 150 °C according to the result of the TG analysis, which limited the reaction temperature. The reaction temperature was increased with an increase in the flow rates of the reactants and decreased with an increase in the flow rate of the carrier gas. The reaction yield decreased with an increase in the flow rate of the carrier gas. 87% yield was obtained with the optimized reaction condition.

Keywords: D. Si_3N_4; Silicon diimide; Silicon nitride; Vapor phase reaction; Imide decomposition

1. Introduction

Silicon nitride has been used in various applications under extreme conditions which include component of valves in internal combustion engines, heat exchangers, cutting tools and gas turbines [1–4], because of the good chemical durability, low density, excellent hardness and high mechanical strength at high temperature. The combination of thermal, dielectric, and superior high-temperature mechanical properties has led to implementation of silicon nitride in electronic applications including electronic substrates, heat sinks, RF waveguides, windows, and radomes [5]. As an indispensable raw material used to prepare silicon-nitride-based ceramics, except for the reaction sintering method, the demands for silicon nitride powder are constantly increasing [6–8].

The quality of the silicon nitride powder can directly affect the performance of silicon nitride ceramic products [9]. At present, several methods are used to produce silicon nitride powder, including (1) direct nitridation of silicon powder, (2) carbothermal reduction and nitridation of SiO_2, (3) self-propagation high-temperature combustion synthesis, (4) chemical vapor-phase reaction method, and (5) thermal decomposition of silicon diimide [10–13]. The first two methods are characterized by long production time, high-energy consumption and low quality of the silicon nitride powder [9]. The self-propagation high-temperature combustion synthesis technology has been applied to the synthesis of various high-temperature materials, including ceramics, intermetallic compounds and composites. It was reported that the silicon nitride powder synthesized by this method was mainly β-Si_3N_4 and it

*Corresponding author at: Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Republic of Korea.
Tel.: +82 2 880 9324.
E-mail addresses: march0321@snu.ac.kr (Y.K. Chung), jaehongkoo@oci.co.kr (J.H. Koo), shinekim@oci.co.kr (S.A. Kim), eunokchi@oci.co.kr (E.O. Chi), jhhahn@oci.co.kr (J.H. Hahn), pchan@snu.ac.kr (C. Park).

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was difficult to control the α/β ratio in the product [14–16]. Sintering mechanism of Si_3N_4 has been reported. Sintering additives such as MgO, Al_2O_3, and Y_2O_3 can react with SiO_2 to form silicates which can exist in liquid phase at the sintering temperature. α-Si_3N_4 powder melts in the liquid phase, β-Si_3N_4 is precipitated, and finally β-Si_3N_4 sintered body is formed by the Ostwald ripening mechanism [17–21]. The nano-size powder synthesized by the chemical vapor-phase reaction in RF plasma is mainly amorphous [22–25]. Nano-size amorphous silicon nitride powder with a high surface energy offers significant advantages in terms of the sintering rate [13,26,27]. In spite of its advantages, the chemical vapor-phase reaction in RF plasma is not suitable for industrial applications because it is not cost-effective for mass production [9,28].

The imide decomposition method is a well-established technology. The imide synthesis reaction takes place at −50–0 °C using liquid-phase reactants [13,29,30]. Most silicon nitride powders which are industrially used are produced by this method. The process, however, consumes a considerable amount of energy. The imide synthesis reaction occurs at extremely low temperature because it uses liquid NH_3 which has very low boiling point of −33 °C. The organic solvent which is used to dissolve $SiCl_4$ must be removed from the reaction product. Furthermore, the handling of liquid ammonia can be very difficult and dangerous as well.

One promising method for the synthesis of silicon nitride powder is the vapor-phase reaction of $SiCl_4$ with NH_3 [31,32]. It is not necessary to use the organic solvent and easy to handle the gaseous reactants using this method. Lange et al. reported that investigations of the vapor-phase reaction between $SiCl_4$ and NH_3 at temperatures of 300–1700 °C showed the formation of extremely fine, spherical and amorphous particles with surface areas up to 300 $m^2\ g^{-1}$[32]. The method, however, has not been industrially used to produce silicon nitride powder because the products grow on the nozzle and are deposited on the reactor wall. It is very difficult to collect the products which have been deposited on the reactor wall and grown on the nozzle. The nozzle can be blocked by the solid products as well [33,34]. The vapor-phase reaction method can be used to produce silicon nitride powder once the problems associated with the reaction products growing on the nozzle and being deposited on the reactor wall are solved. Those problems can be overcome by optimizing the processing conditions. The process parameters of the vapor-phase reaction method, however, have not been systematically investigated or optimized.

In this study, in order to investigate the reaction phenomena and parameters of the vapor-phase reaction, the synthesis and decomposition temperatures of diimide were studied and the effects of the flow rates of the reactants and carrier gas on the reaction temperature, yield, and the particle size were investigated. The heat of the reaction, which can affect the reaction temperature, was calculated. 87% yield was obtained with the optimized reaction condition.

2. Materials and method

The reaction between $SiCl_4$ and NH_3 was carried out at room temperature in a quartz reactor (D100 mm × H500 mm, 4 L). 0.1 mol of $SiCl_4$ and 0.6 mol of NH_3 were introduced into the reactor with separate nozzles, and the reactants were supplied from the bottom to the top of the reactor. Solid products were collected at the bottom of the reactor. The off gas escaped from the top of the reactor. Liquid $SiCl_4$ was vaporized at 150 °C before entering the reactor. Ar was flowed with $SiCl_4$ in order to prevent the condensation of $SiCl_4$, which is necessary to ensure the vapor-phase reaction at room temperature.

The synthesized solid products went through a two-step thermal process to remove the NH_4Cl by-product and decompose diimide to produce amorphous Si_3N_4 in the quartz reactor. The two-step thermal process was carried out immediately after the reaction in the reactor with an electrical tube furnace to prevent the exposure of highly hygroscopic diimide to moisture. The first thermal process to remove the by-product was carried out at 500 °C for 2 h, which was followed by a second thermal process for the decomposition of diimide at 1000 °C for 2 h.

3. Analyses

The prepared powder was characterized by a thermogravimetric analysis (TGA; Mettler Toledo, STAR), a particle size analysis (PSA; BECKMAN COULTER, LS13), and by a scanning electron

Table 1
The yields, tap-densities and mean particle sizes when different flow rates were used.

No.	$SiCl_4$ (ml h^{-1})	NH_3 (ml min^{-1})	Ar (ml min^{-1})	Yield (%)	Tap density (g cm^{-3})		Mean particle size (μm)
					Diimide + NH_4Cl	a-Si_3N_4	
1	6	125	125	97.9	0.21		
2	12	250	250	95.8	0.21	0.11	3.9
3	18	375	375	94.4	0.20		
4	24	500	500	94.1	0.36	0.10	5.3
5	36	750	750	87.3	0.46		
6	48	1000	1000	87.3	0.58	0.12	9.9
7	12	250	1750	48.0	0.28		
8	24	500	1500	74.7	0.49		
9	36	750	1250	78.7	0.59		