J. Am. Ceram. Soc., 94 [12] 4169–4173 (2011)
DOI: 10.1111/j.1551-2916.2011.04914.x


journal

# Rapid Crystallization Process of Amorphous Silicon Nitride

Yanhui Li,[‡] Li Wang,[‡,†] Shaowu Yin,[‡] Fuming Yang,[‡] and Ping Wu[§]

[‡]School of Mechanical Engineering, University of Science & Technology Beijing, Beijing, 100083 China

[§]Department of Physics, University of Science & Technology Beijing, Beijing, 100083 China

**The crystallization of nanosized amorphous silicon nitride powder is one of the methods to produce sub-micrometer/nanosized α-$Si_3N_4$ powder. The application of this method is still limited by the long crystallization time, low output, and high cost. This article invents a new crystallization method of amorphous silicon nitride involving the addition of Si powder. The new process reduces the complete crystallization time from more than 6 h to 30 min, thus allowing efficient production of sub-micrometer/nanosized α-$Si_3N_4$ powder. Effects of factors such as additive, temperature, and duration on the crystallization process are investigated using XRD and FTIR. The experimental results showed that the added Si powder accelerates the crystallization process effectively. The final product is a mixture of α-$Si_3N_4$ and $Si_2N_2O$. In this article, amorphous silicon nitride powder with added Si is annealed at 1450°C. Powder of nearly 100% crystalline phase content is produced either by adding 10% Si and annealing for 15 min or by adding 5% Si and annealing for 30 min.**

## I. Introduction

Silicon nitride ceramics of superior properties have been widely used in the field of energy, metallurgy, machinery, and aerospace industries.[1–3] The quality of the silicon nitride powder directly affects the performance of ceramic productions. Nanosized amorphous silicon nitride powder of high surface energies offer significant advantages in terms of sintering rate.[4–6] In recent years, dense ceramics of more than 90% crystalline phase content were produced by direct sintering of unannealed amorphous powder at temperatures in the range 1600°C–1800°C.[7–10] The amorphous powder exhibits larger shrinkage compared with crystallized ones.[11] The local densification and the formation of clusters happen during sintering connected with the crystallization process.[12]

In the past two decades, several studies on the crystallization process of amorphous silicon nitride powder[13–16] and thin films[17] have been performed. During the crystallization process of micrometer amorphous silicon nitride powder, the chlorine impurities inhibit grain growth, resulting in a delay of the initiation of crystallization. The activation energy calculated using a modified Avrami–Erofe'ev equation is 306 kJ/mol with chlorine impurities and 318 ± 45 kJ/mol without chlorine impurities.[14,15] The ammonium chloride impurites in the silicon nitride powder and the nitrogen in the furnace atmosphere cause the formation of whiskers.[13] A powder of about 80% crystalline phase content with an α/β ratio of about 6 is produced by annealing nanosized amorphous silicon nitride powder at 1450°C for 360 min in nitrogen flow.[16] The XRD result in early research shows that some β-SiC formed and the transformation of α-$Si_3N_4$ to β-$Si_3N_4$ also took place in the amorphous silicon nitride powders after heating at 1700°C.[18]

High quality silicon nitride ceramics are usually produced from pure silicon nitride powder of high α phase content with particle size in the micrometer range and a narrow particle size distribution. Synthesis of nanocrystalline materials from amorphous solids has been proposed for many years.[19–21] The crystallization of nanosized amorphous silicon nitride powder is one of the methods to produce sub-micrometer/nanosized α-$Si_3N_4$ powder. However, in earlier researches, the crystallization process of amorphous silicon nitride is very time consuming. The complete crystallization time of nanosized amorphous powder is more than 6 h at temperatures in the range 1400–1500°C,[16] and the crystallization time of amorphous films is nearly 20 h at 1390°C.[22] The application of this method is still limited by the long crystallization time, low output, and high cost. Developing a means to shorten the crystallization time is a topic of utmost importance from both a theoretic and practical point of view. The aim of this work was to shorten the crystallization time and study the crystallization behavior of amorphous silicon nitride powder with additives.

## II. Experimental Procedures

The additives may accelerate the crystallization process of amorphous powder and shorten the crystallization time. In this respect, special attention should be paid to the effects of additives on the crystallization process of amorphous powder. In this article, α-$Si_3N_4$ and Si powder are chosen as the additives. The added α-$Si_3N_4$ powder may be the seed of the crystallization process as well as the α-$Si_3N_4$ produced by the added Si powder and nitrogen. Characteristics of the raw materials used in the experiments are presented in Table I.

The raw materials are dried in a vacuum oven for 8 h at 100°C to remove adsorbed vapor before crystallization process. The crystallization tests have been performed in a resistance furnace filled with nitrogen gas. The experimental conditions are listed in Table II. The results are analyzed using XRD (Cu-*K*α radiation) and FTIR.

## III. Results and Discussion

### *(1) Effect of Additives Content*

Figure 1 shows the XRD pattern of the product obtained after annealing pure amorphous silicon nitride powder at 1450°C for 90 min (sample A). The diffractogram shows that the amorphous powder did not crystallize. It can be inferred that the crystallization of pure amorphous silicon nitride

H.-J. Kleebe—contributing editor

Manuscript No. 30050. Received July 23, 2011; approved September 19, 2011.
The authors are grateful for the support of the National Natural Science Foundation of China (No. 51076010).
†Author to whom correspondence should be addressed. e-mail: liwang@me.ustb.edu.cn

**Table I. Characteristics of the Raw Materials**

| Raw material | Mean particle size [μm] | Purity [wt%] |
|---|---|---|
| Amorphous silicon nitride | 0.02 | 99.0 |
| α-$Si_3N_4$ | 1 | 99.0 |
| Si | 2.7 | 99.5 |

**Table II. Experimental Conditions**

| No. | Amorphous $Si_3N_4$ [wt%] | Additive | $T$ [°C] | $t$ [min] |
|---|---|---|---|---|
| A | 100 | — | 1450 | 90 |
| B | 95 | α-$Si_3N_4$ | — | — |
| C | 95 | α-$Si_3N_4$ | 1400 | 15 |
| D | 95 | α-$Si_3N_4$ | 1440 | 15 |
| E | 95 | α-$Si_3N_4$ | 1480 | 15 |
| F | 95 | α-$Si_3N_4$ | 1520 | 15 |
| G | 95 | Si | — | — |
| H | 95 | Si | 1400 | 15 |
| I | 95 | Si | 1450 | 8 |
| J | 95 | Si | 1450 | 15 |
| K | 95 | Si | 1450 | 30 |
| L | 95 | Si | 1500 | 15 |
| M | 90 | Si | 1450 | 15 |

powder at 1450°C is very slow, and no obvious phase transformation can be observed after annealing for 90 min. Figure 2 shows the XRD patterns of amorphous silicon nitride powder added with 5% α phase and the product obtained after annealing at 1520°C for 15 min (sample B and F). The diffractograms show that the major phase is still amorphous, and the crystal peaks correspond to the added α-$Si_3N_4$. Other samples added with 5% α phase also show similar results.

Figure 3 shows the XRD patterns of the products obtained after annealing amorphous silicon nitride powder added with 5% and 10% Si at 1450°C for 15 min (sample J and M). Evident crystallization has been observed in both samples. The diffractogram shows that the original amorphous powder has transformed to crystalline phases dominated by α-$Si_3N_4$. Furthermore, $Si_2N_2O$ has been formed because of the adsorbed $O_2$ at the surfaces of amorphous powder and Si powder. The residual Si content decreases with an accompanying nitridation process. The crystalline phase content of sample M is nearly 100%. All reactions involved are shown as follows[16]:

$$\text{amorphous} - Si_3N_4(s) \rightarrow \alpha - Si_3N_4(s) \quad (1)$$

$$3Si(s/l) + 2N_2 \rightarrow \alpha - Si_3N_4(s) \quad (2)$$

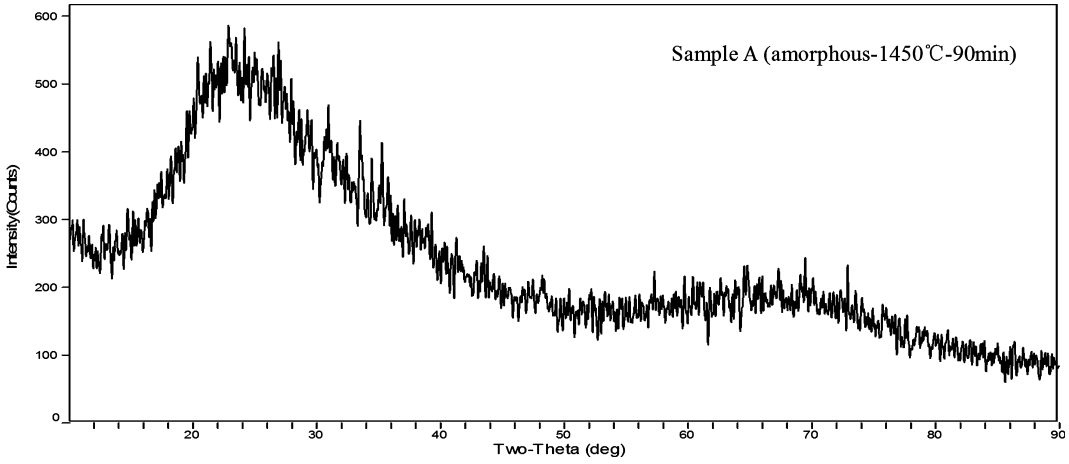


**Fig. 1.** The XRD pattern of sample A, the product obtained after annealing pure amorphous silicon nitride powder at 1450°C for 90 min.

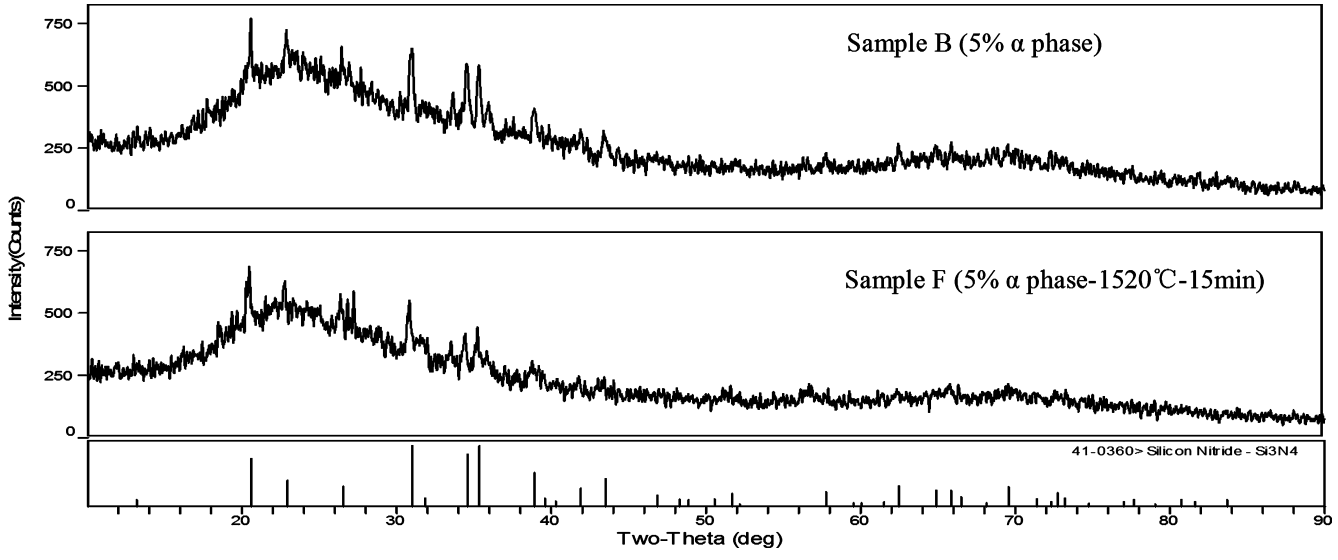


**Fig. 2.** The XRD patterns of amorphous silicon nitride powder added with 5% α phase and the product obtained after annealing at 1520°C for 15 min (sample B and F).

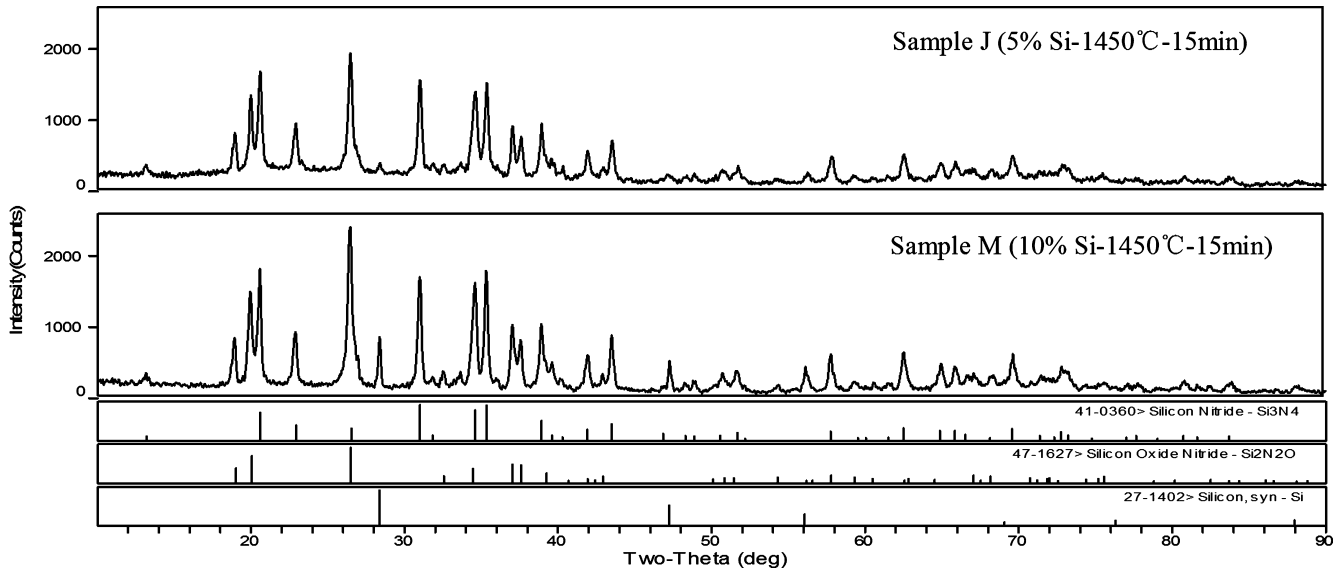


**Fig. 3.** The XRD patterns of the products obtained after annealing amorphous silicon nitride powder added with 5% and 10% Si at 1450°C for 15 min (sample J and M).

$$2Si_3N_4(s) + 1.5O_2(g) \rightarrow 3Si_2N_2O(s) + N_2(g) \quad (3)$$

Figure 4 shows the FTIR spectra of amorphous silicon nitride powder added with 5% Si and the product obtained after annealing at 1450°C for 15 min (sample G and J). It is evident that the main Si–N bond peaks of amorphous silicon nitride centered at 967 $cm^{-1}$ and 474 $cm^{-1}$ have been drastically broadened after heating at 1450°C. In addition, the Si–O bond peak centered at 1083 $cm^{-1}$ disappeared. The remaining "Si–N" peaks may be further decomposed into several separate peaks. The split peaks centered at 853 $cm^{-1}$, 892 $cm^{-1}$, and 981 $cm^{-1}$ correspond to the stretching mode of the Si–N bonds in $\alpha$-$Si_3N_4$ and $Si_2N_2O$. The other two split peaks centered at 461 $cm^{-1}$ and 495 $cm^{-1}$ correspond to the bending mode of the Si–N bonds in $\alpha$-$Si_3N_4$. Comparison between results reveals that the phase transformation process from amorphous powder to $\alpha$-$Si_3N_4$ and $Si_2N_2O$ occurred in sample J.

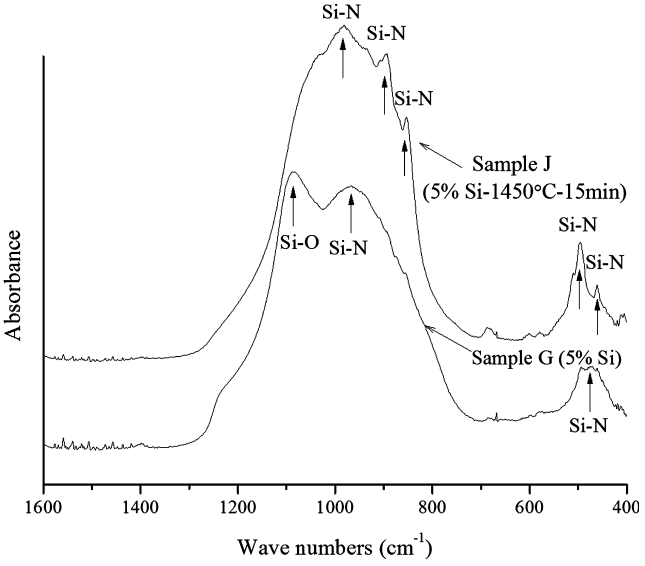


**Fig. 4.** FTIR spectra of amorphous silicon nitride powder added with 5% Si and the product obtained after annealing at 1450°C for 15 min (sample G and J).

The results indicate that the added $\alpha$-$Si_3N_4$ has no evident effect on crystallization process; however, the added Si powder accelerates the crystallization process considerably. Further study is required to understand the reaction mechanism. The added Si powder will react with $N_2$ completely, and the final product will be in a multiphase of $\alpha$-$Si_3N_4$ and $Si_2N_2O$ at the proper conditions.

### *(2) Effect of Temperature*

Earlier research reveals that temperature affects the crystallization significantly.[13] In this study, temperature affects the nitridation of added Si powder as well as the crystallization of amorphous silicon nitride powder.

The XRD patterns of the products obtained after annealing amorphous silicon nitride powder added with 5% Si for 15 min at 1400°C (sample H), 1450°C (sample J), and 1500°C (sample L) are shown in Fig. 5. It can be seen that evident crystallization occurs in the amorphous powder over the entire experimental temperature range. The major phase of the crystallization product is $\alpha$-$Si_3N_4$ and $Si_2N_2O$. The peaks of residual Si can also be observed in the diffractograms. The crystalline phase contents of the three samples are 53%, 77%, and 65%, and the residual Si contents are 1.3%, 0.5%, and 1.1%, respectively. It can be inferred that the crystallization rate of amorphous powder as well as the nitridation rate of added Si at an annealing temerpature of 1450°C is faster than at 1400°C and 1500°C.

### *(3) Effect of Duration*

The products obtained after annealing amorphous silicon nitride powder added with 5% Si at 1450°C for different durations have been labeled as samples I (8 min), J (15 min) and K (30 min). The XRD results are compared in Fig. 6. Evident phase transformation from amorphous to crystalline can be observed even after a short annealing time of 8 min. The residual Si is found after annealing for 8 and 15 min, but disappears after annealing for 30 min. The crystalline phase content of sample K is nearly 100%. It can be inferred that the crystallization process is almost complete after annealing for 30 min which is much shorter than the 6 h reported in the earlier study without the addition of Si powder.[16] Once more, a comparison between results reveals that the added Si powder accelerates the crystallization process considerably. The residual Si content decreases with anneal-

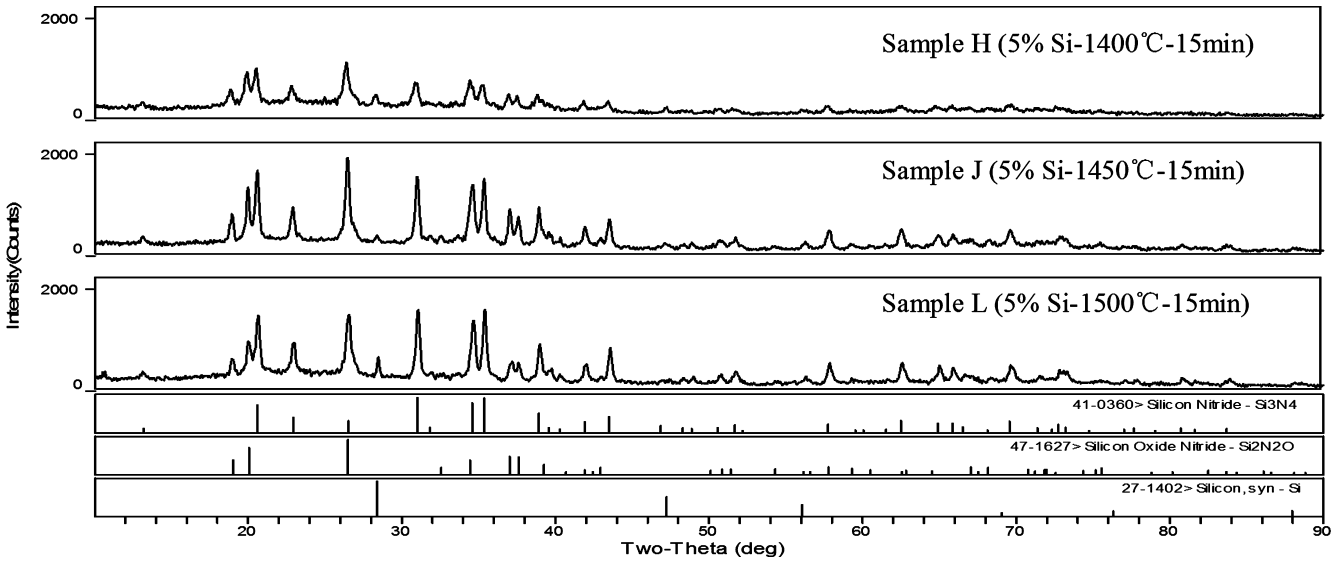


**Fig. 5.** The XRD patterns of the products obtained after annealing amorphous silicon nitride powder added with 5% Si for 15 min at 1400°C (sample H), 1450°C (sample J), and 1500°C (sample L).

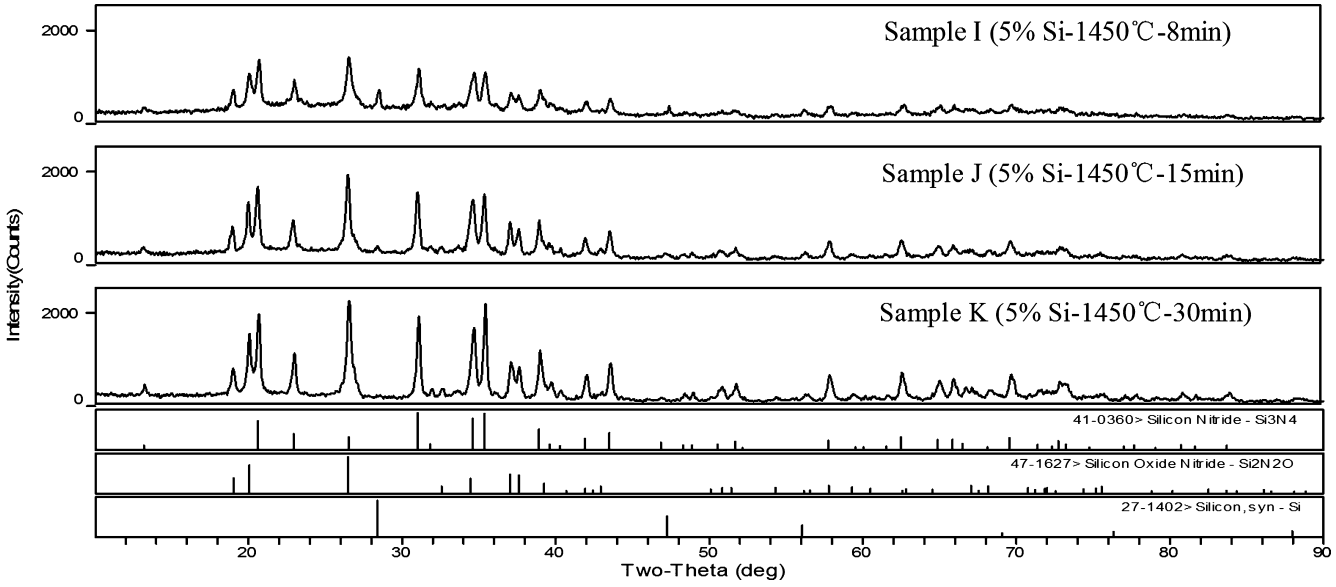


**Fig. 6.** The XRD patterns of the products obtained after annealing amorphous silicon nitride powder added with 5% Si at 1450°C for 8 min (sample I), 15 min (sample J) and 30 min (sample K).

ing time until completely consumed. This reveals that the nitridation of Si occurs simultaneously with the crystallization of amorphous silicon nitride powder. Thus, the added Si powder would transform to $\alpha$-$Si_3N_4$ and the final powder would be in a multiphase of $\alpha$-$Si_3N_4$ and $Si_2N_2O$ without Si impurity.

## IV. Conclusions

In this article, a new crystallization process of amorphous silicon nitride utilizing Si powder additive is proposed. The new process reduces complete crystallization time from more than 6 h to 30 min, thus enabling efficient production of sub-micrometer/nanosized $\alpha$-$Si_3N_4$ powder. The final powder is a mixture of $\alpha$-$Si_3N_4$ and $Si_2N_2O$, because the nitridation of added Si powder and the oxidation of silicon nitride occur simultaneously with the crystallization of amorphous powder. The optimum crystallization temperature of the amorphous powder studied in this work is 1450°C. A final powder of nearly 100% crystalline phase content is produced either by adding 10% Si and annealing at 1450°C for 15 min or by adding 5% Si and annealing at 1450°C for 30 min.

## References

[1]F. L. Riley, "Silicon Nitride and Related Materials," *J. Am. Ceram. Soc.*, **83**, 245–65 (2000).
[2]R. N. Katz, "Applications of Silicon Nitride Based Ceramics," *Ind. Ceram.*, (Italy), **17**, 158–64 (1997).
[3]A. Okada, "Automotive and Industrial Applications of Structural Ceramics in Japan," *J. Eur. Ceram. Soc.*, **28**, 1097–104 (2008).
[4]M. Ziegler, H. Heinrich, and G. Wöttig, "Relationships Between Processing, Microstructure and Properties of Dense and Reaction-Bonded Silicon Nitride," *J. Mater. Sci.*, **22**, 3041–86 (1987).
[5]M. Mitomo, "Thermodynamics, Phase Relations and Sintering Aids of Silicon Nitrede"; pp. 1–12 in *Silicon Nitride-1*, Edited by S. Somiya, M. Mitomo, and M. Yoshimura. Elsevier, London, England, 1990.
[6]J. Szépvölgyi, F. L. Riley, I. Mohai, I. Bertóti, and E. Gilbart, "Composition and Microstructure of Nanosize, Amorphous and Crystalline Silicon Nitride Powders Before, During and After Densification," *J. Mater. Chem.*, **6**, 1175–86 (1996).
[7]J. T. Luo and R. P. Liu, "Effect of Additives on the Sintering of Amorphous Nano-sized Silicon Nitride Powders," *J. Wuhan Univ. Technol. Mater. Sci. Ed.*, **24**, 537–9 (2009).

[8]J. T. Luo, K. F. Zhang, G. F. Wang, and W. B. Han, "Fabrication of Fine-Grained $Si_3N_4$-$Si_2N_2O$ Composites by Sintering Amorphous Nano-sized Silicon Nitride Powders," *J. Wuhan Univ. Technol. Mater. Sci. Ed.*, **21**, 97–9 (2006).

[9]G. T. Burns, J. A. Ewald, and K. Mukherjee, "Hot-Press Sintering Studies of Amorphous Silicon Nitride Powders," *J. Mater. Sci.*, **27**, 3599–604 (1992).

[10]Y. Moriyoshi, M. Futaki, N. Ekinaga, and T. Nakata, "Sintering and Microstructure of Silicon Nitride Prepared by Plasma CVD," *J. Mater. Sci.*, **27**, 4477–82 (1992).

[11]C. Gomez-Aleixandre, J. M. Albella, J. M. Martínez-Duart, and F. Orgaz, "Crystallization and Sintering Characteristics of Chemically Vapor Deposited Silicon Nitride Powders," *J. Mater. Res.*, **7**, 2864–8 (1992).

[12]H. T. Sawhill and J. S. Haggerty, "Crystallization of Ultrafine Amorphous $Si_3N_4$ During Sintering," *J. Am. Ceram. Soc.*, **65**, c131–2 (1982).

[13]F. Allaire and R. Langlois, "Factors Influencing the Crystallization of Ultrafine Plasma-Synthesized Silicon Nitride as a Single Powder and in Composite SiC-$Si_3N_4$ Powder," *J. Mater. Sci.*, **27**, 1265–70 (1992).

[14]R. Riedel and M. Seher, "Crystallization Behaviour of Amorphous Silicon Nitride," *J. Eur. Ceram. Soc.*, **7**, 21–5 (1991).

[15]M. Seher, J. Bill, F. Aldinger, and R. Riedel, "Crystallization Kinetics of Polysilazane-Derived Amorphous Silicon Nitride," *J. Cryst. Growth*, **137**, 452–6 (1994).

[16]J. Szépvölgyi and I. Mohai, "Crystallization of an Amorphous Silicon Nitride Powder Produced in a Radiofrequency Thermal Plasma," *Ceram. Int.*, **25**, 711–5 (1999).

[17]N. Jehanathan, M. Saunders, Y. Liu, and J. Dell, "Crystallization of Silicon Nitride Thin Films Synthesized by Plasma-Enhanced Chemical Vapour Deposition," *Scripta Mater.*, **57**, 739–42 (2007).

[18]Y. Li, Y. Liang, F. Zheng, X. Shong, and Z. Hu, "Phase Transition and Particulate Growth of Laser Synthesized Ultrafine Amorphous Silicon Nitride Powders," *J. Mater. Sci. Lett.*, **13**, 1588–90 (1994).

[19]H. Gleiter, "Nanocrystalline Materials," *Prog. Mater. Sci.*, **33**, 223–315 (1989).

[20]R. Birringer, U. Herr, and H. Gleiter, "Nanocrystalline Materials-A First Report, Transactions of Japan Institute of Metals," *Trans. Jpn. Inst. Met. Suppl.*, **27**, 43–52 (1986).

[21]K. Lu, "Synthesis of Nanocrystalline Materials from Amorphous Solids," *Adv. Mater.*, **11**, 1127–8 (1999).

[22]H. Schmidt, W. Gruber, G. Borchardt, M. Bruns, M. Rudolphi, and H. Baumann, "Thermal Stability and Crystallization Kinetics of Sputtered Amorphous $Si_3N_4$ Films," *Thin Solid Films*, **450**, 346–51 (2004). □