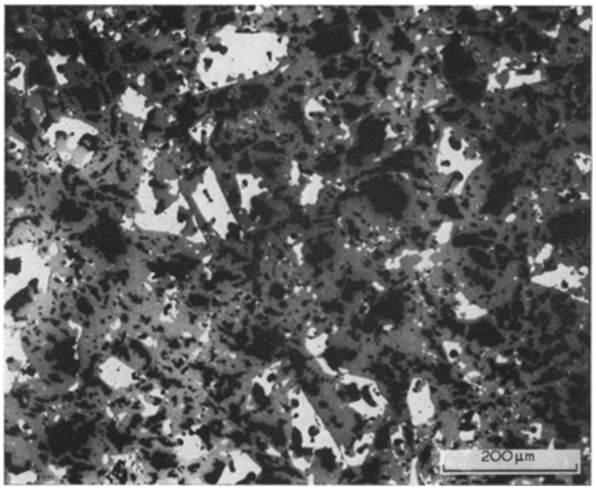

Figure 3 Optical micrograph of a polished section of a compact nitrided for 60 h at 1360°C and 0.067 bar. (White, silicon; grey, nitride; black, porosity).

different nitrogen pressures. The curves show three distinct regions. Initially, the kinetics are linear, then the rate decreases until, finally, nitridation effectively ceases. Although the linear rate increases with increasing nitrogen pressure, the most interesting feature is that more nitride is eventually produced at lower nitrogen pressures.

Fig. 2 is a scanning electron micrograph of the surface of a silicon slice after reaction at 0.067 bar in the regime of linear kinetics. It shows the surface of the silicon to be only partially covered with nitride. It is thought that the gradual departure from linear kinetics is related to the progressive occlusion of the silicon surface until finally, with complete coverage, the nitridation rate becomes negligible. That this coverage is attained more rapidly at higher nitrogen pressures is probably related to the associated increases in the nitride nucleation rate and density.

The microstructure of a compact nitrided to this final stage is shown in Fig. 3. The nitride formed amounts to 75% conversion of the original 75 to 100 µm particles. From this it is estimated that pure particles of up to 30 µm diameter may be nitrided completely using low nitrogen pressures. A characteristic feature of this reaction is the occurrence of pores within the silicon particles (Fig. 3). It was evident from examination of the single crystal and the compacts that the pores were formed by the evaporation or surface diffusion of silicon from uncovered areas of the surface. Furthermore, the transport of both silicon and nitrogen was via gaps in the nitride deposit and not by solid-state diffusion as previously thought likely [1].

Acknowledgement

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Synthesis of the α form of silicon nitride from silica

The synthesis of silicon nitride powders by reaction between silica, carbon and nitrogen has been well known since a German patent was granted in 1896 to Mehner [1]. However, the reaction seems to be more complicated than the reaction between silicon and nitrogen elements, which is generally used for the production of commercial silicon nitride, because of the simultaneous formation of silicon oxynitride (Si_2ON_2), silicon carbide (SiC) and the existence of unreacted silica. Because of the wide availability of silica and carbon of very high purity and fine particle size from commercial sources,

TABLE I Nitrogen analysis of some samples prepared by silica reduction

Raw powder		C/silica (molar ratio)	Heating condition		Nitrogen content (wt %)
Silica	Carbon		Temperature (°C)	Time (h)	
(A)	Lamp black	20	1400	5	26.8
				10	32.3
				20	34.1
(B)	Lamp black	20	1400	5	33.7
				10	35.3

TABLE II Change in total weight and total silicon content in nitriding reaction (residual carbon is included)

Raw powder		C/silica (molar ratio)	Weight loss (%)			$\frac{\text{Total silicon after heating}}{\text{Total silicon before heating}}$ (%)	
Silica	Carbon		Calculated*	1000°C, 5 h	1400°C, 5 h	1000°C, 5 h	1400°C, 5 h
(A)	Lamp black	2	55.6	8.4	30.5	100.9 (+ 0.9)	94.4 (− 5.6)
(A)	Lamp black	20	11.5	5.4	15.4	100.9 (+ 0.9)	86.2 (− 13.8)

*Calculated values based on the reaction: $3SiO_2 + nC + 2N_2 \rightarrow Si_3N_4 + 6CO + (n - 6)C$

the reaction by reduction of silica is expected to produce high purity, fine silicon nitride powder. As Wild *et al.* [2] described, the α form of silicon nitride is an oxynitride, $Si_{11.5}N_{15}O_{0.5}$, with oxygen replacing nitrogen in some sites. Therefore, the reduction reaction from silica seems to be applicable for making α silicon nitride with high purity.

In the present investigation, synthesis experiments on α silicon nitride powder by reduction of silica in a nitrogen atmosphere were carried out using various thermal treatment conditions and compositions of silica and carbon. Two types of high purity fine amorphous silica, types A and B, whose specific surface areas were 1.72 m^2 g^{-1} and 300 ± 30 m^2 g^{-1}, respectively, and high purity lamp black carbon, whose specific surface area was 95 m^2 g^{-1}, were mixed by wet ball milling. A graphite crucible was used as a sample container and the experiments were carried out in the temperature range 1000 to 1500°C in nitrogen gas (flow rate: 2 l min^{-1}). The excess carbon of the reaction products was burned off in air at 600°C for 8 h. Nitrogen and silicon analysis of the products was performed by acid-base titration after alkali fusion and molybdenum spectrophotometry, respectively. X-ray diffraction and scanning electron microscopy were also used to investigate the nature of the product.

The appropriate temperature for α silicon nitride formation was in the range 1400 to 1450°C. At 1500°C, silicon carbide was apparently formed. This result coincided well with the work of Kijima *et al.* [3]; however, Cutler [4] indicated 1350°C as the maximum preparation temperature. Table I shows typical nitrogen contents of the reaction products. The reaction rate was enhanced with increasing the surface area of raw powders. Fig. 1 shows the variations of nitrogen content with carbon-to-silica molar ratio for powders prepared by heat-treatment at 1400°C for 5 h in a nitrogen gas flow of 2 l min^{-1}. Experimental accuracy has been con-

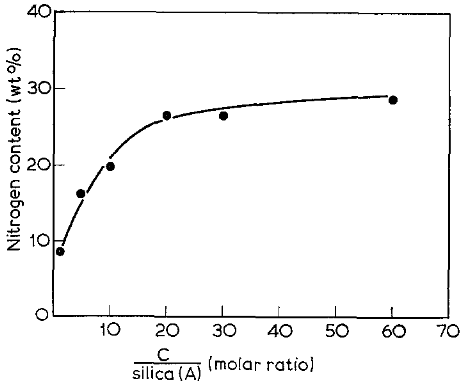

Figure 1 Relations between nitrogen content and C/silica (A) in powders prepared by heating at 1400°C for 5 h in nitrogen gas (2 l min^{-1}).

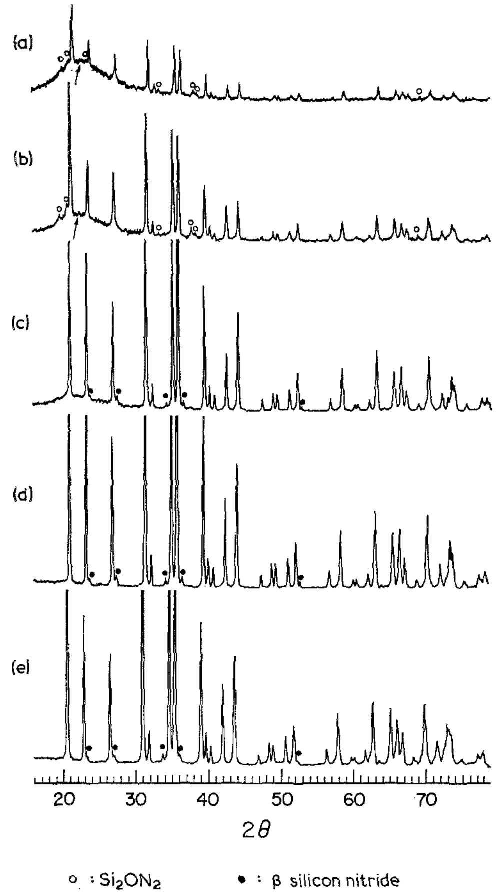

Figure 2 X-ray diffraction patterns of typical synthesized α silicon nitride (graphite crystal-reflected monochromatic Cu*K*α, 50 kV 80 mA, full scale 2000 cps). (a) C/silica (A) (molar ratio) = 2, heated at 1400°C for 5 h. (b) C/silica (A) = 5, heated at 1400°C for 5 h. (c) C/silica (A) = 20, heated at 1400°C for 5 h. (d) C/silica (A) = 20, heated at 1400°C for 20 h. (e) C/silica (B) = 20, heated at 1400° C for 10 h.

firmed by examining mixing condition effect on the reduction reaction. The silicon nitride formation rate was largely affected by the initial carbon-to-silica molar ratio, i.e. the reaction rate significantly increased with increase in carbon content, from the theoretical molar ratio (C/silica $\simeq$ 2) to 20. The silicon nitride formation by reduction from silica was assumed to include a vapour-phase reaction between silicon monoxide and nitrogen in the presence of carbon, as in the following equations:

$$\mathrm{SiO_2(S) + C(S) = SiO(S) + CO(G)} \quad (1)$$

$$\mathrm{SiO(S) = SiO(G)} \quad (2)$$

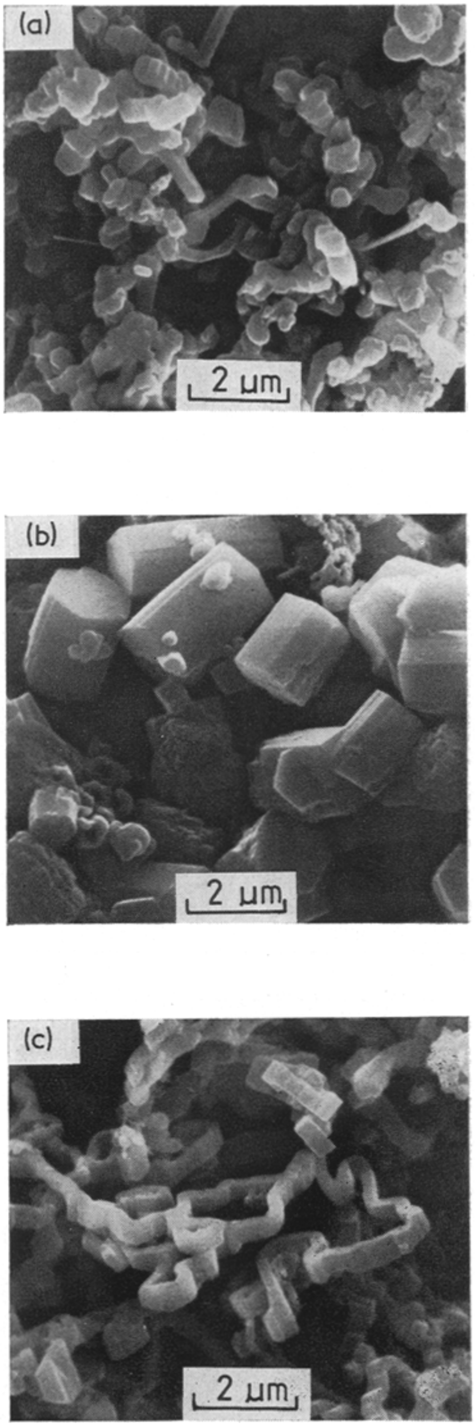

Figure 3 Scanning electron micrographs of typical synthesized products. (a) C/silica (A) = 20 (molar ratio), heated at 1400°C for 5 h. (b) C/silica (A) = 20, heated at 1400°C for 10 h. (c) C/silica (B) = 20, heated at 1400°C for 5 h.

$$3SiO(G) + 3C(S) + 2N_2(G) = Si_3N_4(S) + 3CO(G) \quad (3)$$

The result shown in Fig. 1 means that excess carbon might be an essential component to give more chances for oxygen reduction from silicon monoxide vapour.

Table II shows typical weight loss and variation of total silicon in nitriding reaction. Silicon was not responsible for the total weight loss of 5 to 9% in the heat-treatment at 1000° C, in which silicon nitride was not formed. On heating, a small amount of silicon was lost, presumably in the form of silicon monoxide. The results in Table II and Fig. 1 indicated that at low C/silica ratio (2 to 10), considerable amounts of silica and silicon monoxide remained unreacted after heating at 1400° C for 5 h.

Figs. 2 and 3 show X-ray diffraction patterns and micrographs of typical reaction products, respectively. The X-ray diffraction patterns indicated that lower nitrogen content powder products contained residual unreacted silica (arrow) and a small amount of Si_2ON_2. On the other hand, high nitrogen powders gave sharper diffraction lines of α silicon nitride than low nitrogen content ones. The shape of the powder product after reaction was different from that of raw silica powder, which had a granular shape with irregular surfaces, i.e. initial-stage reaction products with a lower nitrogen content, were rather fibrous in shape and small in size, and the shape of the products gradually changed from fibrous to granular with increasing nitrogen content. This behaviour might be evidence that the vapour-phase reaction had occurred during the silicon nitride formation process. The grains of the final product with a high nitrogen content were in the shape of hexagonal columns.

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On the thermoluminescence of X-ray irradiated polycrystalline Al_2O_3 powder

Ceramics are of utmost importance in advanced technology and hence the studies of their properties are of great interest. Attempts have been made to understand the effect of radiation on ceramics, especially on Al_2O_3 in various forms, e.g. single crystals, flakes, powders. More recently, attempts have been made to use ceramics as radiation dosimeters by utilizing their thermoluminescence output. Thermoluminescence is generally used in studying the electron and hole traps in solids and also in understanding the radiative recombinations and related electronic processes. The thermoluminescence of γ-irradiated α-Al_2O_3 crystals has been studied by several workers [1-5] and the main glow peaks are well known. The coloration induced in single crystals of corundum (Al_2O_3) by X-rays has been investigated by Hunt *et al.* [6] and that induced by γ-rays has been studied by Levy [7]. The electronic processes in α-Al_2O_3 crystals are now well understood. However, sufficient information about the effect of X-rays on polycrystalline Al_2O_3 powder is absent from the literature. Rieke *et al.* [8] studied the thermoluminescence of γ-irradiated Al_2O_3 powder and, more recently, Galli [9] has investigated the defects produced in the reactor-irradiated polycrystalline α-Al_2O_3 by E.P.R. measurement. Ziniker *et al.* [5] and Buckman [10] have proposed the potential use of α-Al_2O_3 crystals as a thermoluminescent dosimeter for X-rays. But to the best of the author's knowledge, no work has been reported on the possibility of using polycrystalline Al_2O_3 powder as X-ray dosimetry material. The purpose of this work is to investigate the thermoluminescent output of polycrystalline Al_2O_3 powder.