

Production of silicon nitride by gas nitridation of ultra-fine silicon powder

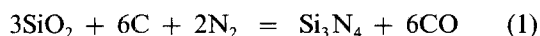
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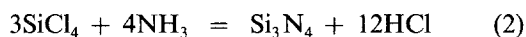
Ultra-fine silicon powder of diameter 20 to 50 nm was gas nitrided at 1373 K. Contamination with air increased the nitriding temperature, which was lower than that found in previous work for larger particle-size powders.

1. Introduction

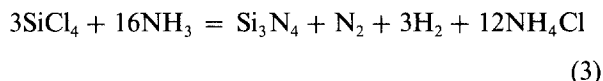
Silicon nitride powders have been produced by many methods, one of which is the reduction of silica, which uses a reaction such as



Silicon halide (typically chloride) is also used to produce silicon nitride in the gas and liquid phase. In the gas phase, we have



and in the liquid phase,



Another common method reported is the gas nitriding of silicon powder of 15 to 8 μm diameter at a temperature between 1520 and 1720 K under nitrogen and hydrogen atmospheres [1-3].

Chemical vapour deposition (CVD) of halogen nitride, may also be used. The difficulty of this method is to remove the residual halogen. One of the methods of silicon nitride and also titanium nitride production was described by Yoshida *et al.* [4]. A very fine silicon nitride powder of 17 nm was also produced by a laser reactor; however, the problems of small productivity and the treatment of poisonous silane remain to be solved [5, 6]. Kijima [7] reviewed some methods of production of silicon nitride. We compared the productivity of these methods with that of arc plasma equipment, and concluded that the most efficient method is that of arc plasma [8].

In the present work silicon powder was produced by our arc plasma equipment [8], then the metallic silicon powder was nitrided.

2. Experimental procedure

Ultra-fine silicon powder of 20 to 50 nm was used in this work. The method of production has been described elsewhere [8].

Some batches of the powder produced were nitrided directly after collecting on a mullite filter which was located in an atmosphere-controlled chamber of the silicon production furnace; others were nitrided after 24 h exposure to air to evaluate the effects of air

contamination, which simulated normal production or experimental procedure reported previously in other works. The nitriding conditions were under a nitrogen and hydrogen flow of 100 and 5 ml min^{-1} hydrogen, respectively. The sample was exposed to a nitriding temperature at a heating rate of 0.25 K sec^{-1} , and kept at the nitriding temperature for 1 h.

The samples were examined semi-quantitatively by X-ray diffraction to evaluate the degree of nitriding by using a correction of the mass absorption coefficients [9]. The particle size of the products was measured by a TEM. Chemical bondings were also examined by infrared spectrometry.

3. Results

The silicon powder not exposed to air was ready to nitride at lower temperatures, whereas the air-contaminated powder required higher nitriding temperatures. Typical X-ray diffraction patterns of nitrided samples are shown in Figs 1a and b for nitriding temperatures of 1373 and 1473 K, respectively. Unexposed clean samples and air-exposed contaminated samples are compared. Open circles correspond to the diffraction of $\alpha\text{-Si}_3\text{N}_4$. The clean and air-exposed samples were nitrided at 1373 and 1473 K, respectively. The air-exposed samples could not be nitrided at 1373 K.

The weight percentages of silicon nitride and crystalline silicon in nitrided silicon powder at various

TABLE I Percentage of Si and $\alpha\text{-Si}_3\text{N}_4$ by X-ray diffraction intensity nitrided at different temperatures, using clean or air-contaminated silicon powder

Samples	Temperature (K)	$\alpha\text{-Si}_3\text{N}_4$ (wt %)	Si (wt %)	Fig. no.
Clean	1473	60	N	Fig. 2a
	1423	39	4	Fig. 2b
	1373	23	20	Fig. 2c
	1323	N	30	
Air-contaminated	1623	41	N	
	1573	38	N	Fig. 2d
	1473	36	3	Fig. 2e
	1423	N	33	
	1373	N	37	Fig. 2f

N: not found.

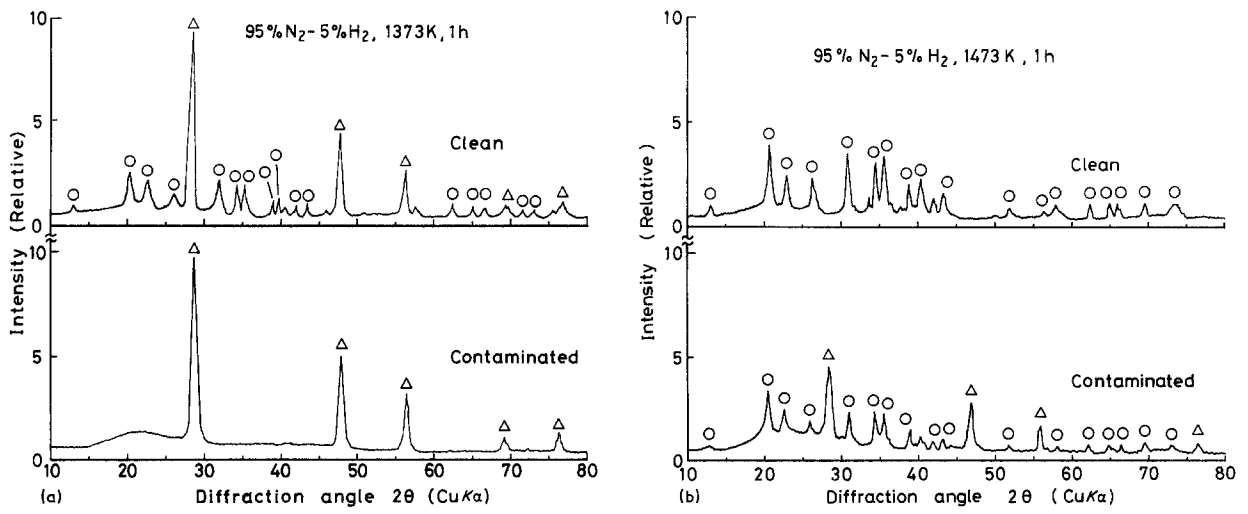


Figure 1 X-ray diffraction pattern of silicon powder nitrided at (a) 1373 K, and (b) 1473 K. Clean samples not exposed to air and air-exposed contaminated samples are compared. (Δ) (\circ) Corresponding diffraction of silicon and α - Si_3Ni_4 , respectively.

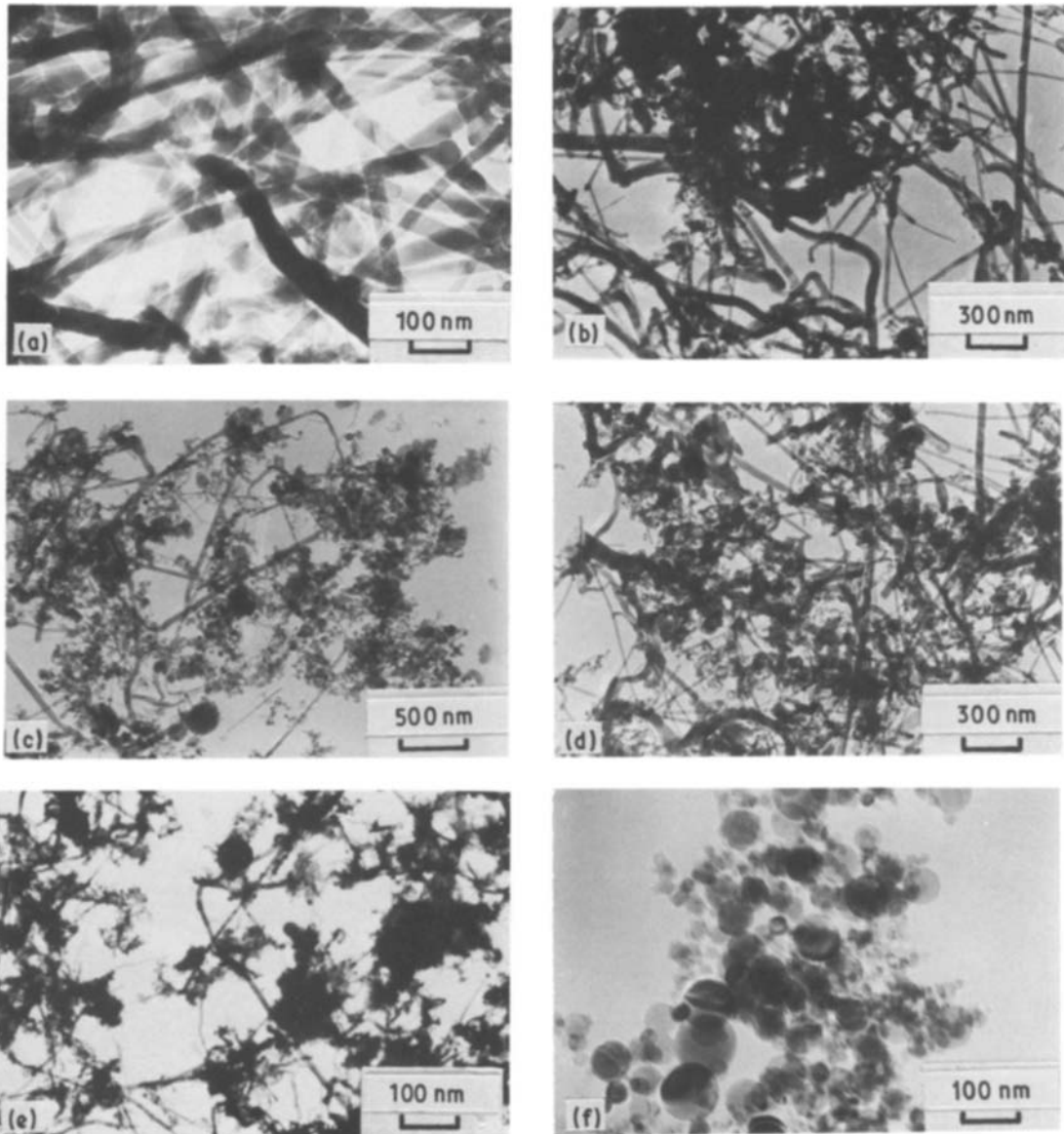


Figure 2 Transmission electron micrographs of nitrided silicon powder. Nitriding temperature and nitrided products are shown in Table II. The ribbon-shaped crystals are silicon nitride.

nitriding temperatures are listed in Table I. The rest of the material is amorphous silicon nitride or other impurities. The concentration was estimated by relative X-ray intensity of the nitrided samples in comparison with a standard mixture specimen of silicon powder (97.5% purity, particle size 2.7 μm) and silicon nitride (97% purity, more than 98% α -phase, particle size 860 nm). Some of the transmission electron micrographs are also shown in Fig. 2. The silicon nitride powder has the tendency to form a fibre or agglomerated form as shown in Fig. 2a. The electron diffraction pattern revealed the fibre to be α - Si_3N_4 and the other form is amorphous.

The chemical bonds of Si-N and Si-O were examined by infrared spectroscopy. Fig. 3 shows the spectra of KBr-based material, commercial silicon nitride, air-contaminated silicon nitrided at 1573 K, and clean silicon powder nitrided at 1473 K. The air-contaminated sample shows strong Si-O peaks (1020 to 1090 cm^{-1}). Strong spectra of Si-N were also found in all the samples.

4. Discussion

Silicon nitride powder was previously produced by gas nitriding silicon powder of rather large particle size, i.e. 15 to 3 μm diameter. The nitriding temperature ranged between 1573 and 1723 K under a nitrogen and hydrogen atmosphere, e.g. at a temperature of 1573 to 1673 K [1], between 1603 and 1723 K for 3 to 8 μm particles [2], and for silicon powder of about 8 μm diameter nitrided at 1623 K after pretreatment in hydrogen at 1123 K [3].

Silicon nitride was formed in ribbon-like shaped crystals as seen in Fig. 2. One of the possibilities to form this shape is the gas-phase reaction of SiO vapour. However, the formation of SiO vapour is insignificant up to about 1700 K as seen in Fig. 4.

The next possibility is by the vapour of solid silicon for



The vapour pressure of silicon at 1600 K is about

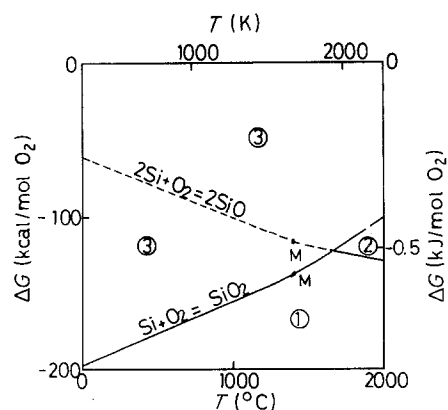


Figure 4 Free energy of formation per 1 mol O_2 plotted against temperature, where M corresponds to the melting point of silicon. Regions 1, 2 and 3 correspond to silicon, silicon monoxide and SiO_2 , respectively, as a stable phase. The gas phase of silicon monoxide is stable above 1700 K at the lowest estimated temperature.

10^{-2} Pa [10], at which point normal particles of about 10 μm were nitrided. On the other hand, our samples of 20 to 50 nm powder were nitrided at about 1400 K, at which temperature the vapour pressure of silicon is about 10^{-4} Pa [10]. The vapour pressure of silicon cannot be increased from 10^{-4} to 10^{-2} Pa by the reduction of the powder size. The pressure change could be a few points at the most for the reduction of diameter considered [11]. Thus the vapour pressure difference due to the reduction of diameter is not a valid reason for the lower nitriding temperature. Therefore, the reaction is not controlled by the silicon vapour pressure. The reason for the reduction of nitriding temperature may be due to some kinetic factors and not thermodynamic ones.

Air-contaminated samples had strong Si-O bonds as seen in Fig. 3, and the nitriding temperature was higher. This means that the surface phase had a different structure after air contamination. The air-contaminated surface was less active.

Smaller particles are becoming more and more common, so air contamination will be an important problem in the future. This work also reports the lowest

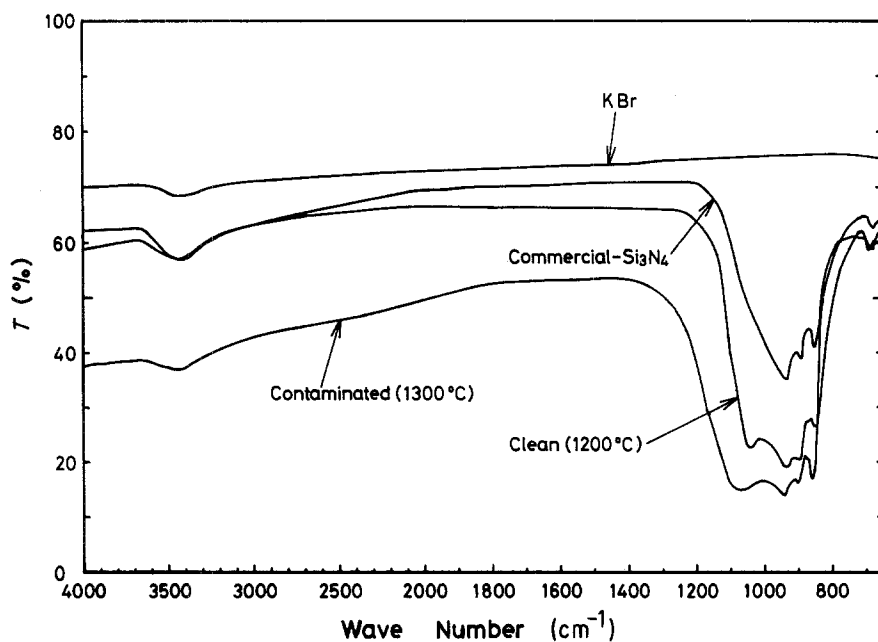


Figure 3 Infrared spectroscopy of chemical bonds of Si-N and Si-O. Base material, KBr; commercial silicon nitride, air-contaminated silicon nitrided at 1573 K, and clean silicon powder nitrided at 1473 K. The air contaminated sample shows strong Si-O peaks (1020 to 1090 cm^{-1}).

temperature of nitriding. The smaller particles have the advantage of a lower nitriding temperature.

5. Conclusion

Ultra-fine nitrided silicon powder or agglomerated fibres of approximately 50 nm diameter and 1 μ m length were produced by nitriding the powder directly without exposure to air. This is the smallest gas-nitrided silicon powder reported. Previous work nitrided silicon powder of 800 nm to 3 μ m. The nitriding was very short and fast at 1373 K for the present work, which is at a lower temperature than in any other work reported. This reduction of nitriding temperature is attributed to the small diameter of the silicon powder used here, and the nitriding process was conducted directly without considerable air contamination, unlike in previous work. The effect of air contamination cannot be neglected, especially for these ultra-fine powders. The powder has a tendency to form fibres after nitriding treatment.

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*Received 10 August
and accepted 22 October 1987*