JOURNAL OF MATERIALS SCIENCE 19 (1984) 189–194

The removal of surface silica and its effect on the nitridation of high-purity silicon

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Compacts of high-purity silicon powder were pretreated in hydrogen or argon to remove the surface silica and then nitrided in gas at atmospheric pressure and at 1623 K. The kinetics of nitridation were monitored continuously, the fracture surfaces of the nitrided samples examined using scanning electron microscopy and the alpha/beta nitride contents determined by X-ray diffraction. The experiments confirm that high-purity silicon powder, usually regarded as unreactive, can be rapidly nitrided to nearly complete conversion following pretreatments designed to remove the silica layer. The results suggest that nitridation occurred by the reaction of silicon vapour with nitrogen gas resulting in the deposition of massive Si_3N_4.

1. Introduction

In studies of the mechanisms of nitridation of silicon and in the preparation of high-purity silicon nitride powder and reaction-bonded silicon nitride (RBSN), it is essential that the starting silicon powder is low in impurities such as iron and aluminium [1]. In this respect silicon powder made from semi-conductor grade silicon has been used. A major contaminant in any silicon powder, however, is oxygen present as a thin (typically ~ 3 nm) native oxide layer covering the surface of the silicon particles. It is well established that this oxide layer has a pronounced retarding effect on nitridation kinetics and that pretreatment of the powder with the object of removing the layer leads to accelerated kinetics [2–4].

A major limitation of studies involving pretreatments reported by other authors is that most kinetics have been obtained in intermittent experiments and, even when the kinetics were monitored continuously, they covered only the very initial stages of the nitridation process.

In an earlier publication [5] the present authors reported the initial results of a study of the effects of pretreatments on the nitridation kinetics of high-purity silicon powder. The present paper reports the results of experiments with and without the pretreatment stage for (i) the kinetics of nitridation for different mixtures of nitrogen and hydrogen in the nitriding gas, (ii) the α and β silicon nitride contents of the nitrided compact, and (iii) the morphology of the silicon nitride as revealed by scanning electron microscopy of fracture surfaces.

Such results are important not only for the understanding of the mechanisms of nitridation but also for the preparation of high-purity silicon nitride powder and RBSN. Furthermore, the data are important to studies of the densification of RBSN where a high-purity starting material will allow the possibility of meaningful experiments to determine the effects of additives.

2. Experimental procedure

2.1. Materials and preparation

The method of preparation of the high-purity silicon powder has been described elsewhere [6]. Analysis both by chemical methods† and by X-ray fluorescence‡ determined impurity levels of iron and aluminium to be at 60 ppm and < 30 ppm, respectively. The powder was compacted isostatically at 200 MN m^{-2} into pellets 10 mm

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diameter by 10 mm long. The particle size of the powder was $< 8\,\mu m$.

2.2. Apparatus

The controlled atmosphere thermogravimetric balance used for the pretreatment and nitriding experiments has been described elsewhere [6]. The balance incorporated a facility for raising and lowering the sample which was contained in a small perforated alumina crucible. The oxygen and water contents of the nitriding gases were monitored and were typically close to 10 ppm. All pretreatment and nitriding experiments were carried out in flowing gases at atmospheric pressure, the flow rate of the gases being controlled and measured using flowmeters.

2.3. Pretreatment and nitriding schedules

With the hot zone of the furnace at the reaction temperature (1623 K in all experiments) a sample was positioned high in the balance where its temperature was less than 373 K and the system pumped down to a pressure of $\sim 10^{-2}$ mm Hg. The system was left purging for ~ 12 h. The pretreatment gases (argon or hydrogen) were then passed into the balance and a flowrate of $\sim 100\,\text{ml min}^{-1}$ established. This gas flow was maintained for ~ 6 h after which the sample was lowered into the hot zone for a pretreatment of 1 h. The weight loss during the pretreatment, due to the removal of the native oxide layer, was recorded.

After the pretreatment stage, the sample was raised to a higher point in the system where its temperature was ~ 1123 K. The pretreatment gas was then turned off and the nitriding gas turned on. Thus the pretreatment gas was replaced by the nitriding gas, while still maintaining a low (~ 10 ppm) oxygen content in the system. Furthermore, during this stage the sample was kept at a temperature low enough to prevent nitridation but high enough to prevent reoxidation of the cleaned silicon surface. After 2 h, and having established a gas flow rate of $100\,\text{ml min}^{-1}$, the sample was lowered into the hot zone and the weight gain continuously measured. The nitriding gases used were nitrogen, nitrogen/5% hydrogen, or nitrogen/50% hydrogen.

For comparison, nitriding experiments without any pretreatment were also performed. In these experiments, after the balance was evacuated, the nitriding gas (nitrogen or nitrogen/5% hydrogen) was admitted and the flow rate of $100\,\text{ml min}^{-1}$ established and maintained for ~ 6 h. The sample was then lowered into the hot zone and the weight gain continuously monitored.

2.4. Microstructural analysis

Fracture surfaces of nitrided samples were examined in the scanning electron microscope. For X-ray diffraction studies samples were ground to a fine powder. The amounts of α and β silicon nitride and unreacted silicon were obtained following the procedure described by Gazzara and Messier [7].

3. Results

Preliminary experiments showed that the effects of rate of flow of nitriding gas into the compact and self-heating of the compact were unimportant; after pretreatment, the kinetics of nitridation of uncompacted silicon powder were similar to those of a compact of the same mass. Examination of nitrided compacts under a low power microscope showed a uniform colour and texture. These observations are in accordance with previous work [8,9].

Weight losses during pretreatment showed that the silicon powder contained ~ 1.5 wt% silica on its surface. In hydrogen removal of the silica layer was completed within 0.5 h while in argon removal was completed within 1 h.

All pretreatment and/or nitriding experiments were repeated. Reproducibility of the results for the kinetics of nitridation and for the α and β-silicon nitride contents were excellent, to within 5%.

3.1. Nitridation kinetics

Fig. 1 shows the results for the percentage nitridation plotted against time for samples which were nitrided following pretreatment. It is seen that pretreatment in argon containing a low oxygen content is effective. For nitridation in nitrogen and nitrogen/5% hydrogen the kinetics were extremely rapid, with the compacts achieving nitridation levels of > 95% in less than 1 h. The dependence of the nitridation rate on the nitrogen content of the nitriding gas is clearly seen from the results for the experiment in nitrogen/50% hydrogen.

Fig. 1 also shows the results for the percentage nitridation of silicon plotted against time for samples which were not pretreated. In nitrogen/5% hydrogen the compacts achieved a nitridation level of ~ 95% after 1 day. In nitrogen the kinetics were extremely slow, the compacts achieving ~ 30% nitridation after 1 day.

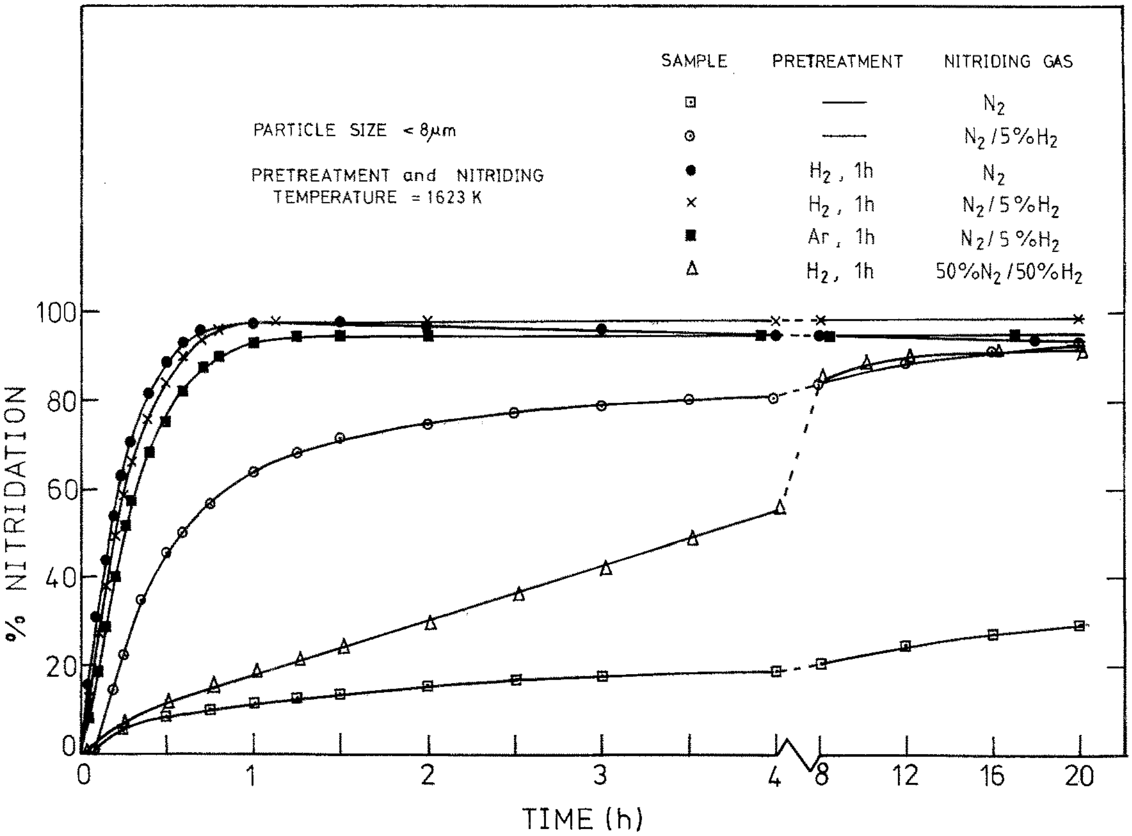

Figure 1 Percentage nitridation plotted against time for samples nitrided following pretreatment in hydrogen or argon for 1 h and for samples nitrided without pretreatment.

3.2. α/β phase contents

Fig. 2 shows the α- and β-silicon nitride phase contents plotted against nitriding time for samples which were pretreated in the hydrogen, then nitrided in nitrogen/5% hydrogen. The data obtained after nitriding for 1 h, when the reaction was complete, were the same as those after nitriding for 1 day, confirming that there was no conversion of α- to β-nitride.

Fig. 3 shows the results for samples nitrided in nitrogen/5% hydrogen without pretreatment. It appears that the reaction forming β nitride stops after ~ 1.5 h but the α-forming reaction continues to the end.

The percentage nitridation calculated from X-ray analysis is in good agreement with the results obtained from weight gain measurements. The largest difference occurred for the case of nitridation to > 90% in nitrogen/50% hydrogen following pretreatment. In this case the value obtained from X-ray analysis was ~ 5% higher than that obtained from weight gain measurements. There appeared to be a small weight loss during the relatively slow reaction.

Table I summarizes the determined phase compositions.

It is seen that having removed the native silica layer by pretreatment, the α- and β-nitride contents (~ 81% α, ~ 17% β) are the same after nitridation in the different gas mixtures. These values are not, however, very different from those (75% α, 20% β) for the sample nitrided in nitrogen/5% hydrogen without pretreatment.

TABLE I Phase compositions after 24 h nitriding

Pretreatment	Nitriding gas	α (%)	β (%)	Si (%)
H_2	N_2	83	15	2
H_2	$N_2/5\%\ H_2$	82	17	1
Ar	$N_2/5\%\ H_2$	81	17	2
H_2	$50\%\ N_2/50\%\ H_2$	79	16	5
–	N_2	29	3	68
–	$N_2/5\%\ H_2$	75	20	5

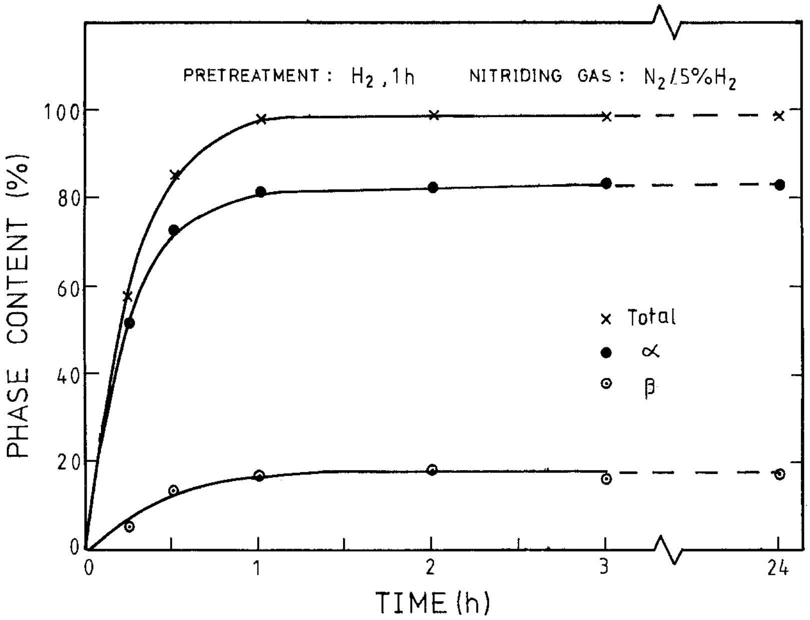

Figure 2 α- and β-silicon nitride phase contents plotted against time for samples pretreated in hydrogen for 1 h, then nitrided in nitrogen/5% hydrogen.

3.3. Morphology of fracture surfaces

Fig. 4 shows the scanning electron micrographs of a sample pretreated in hydrogen then nitrided in nitrogen/5% hydrogen. These are indistinguishable from the micrographs obtained from the other nitriding conditions following pretreatment. The massive morphology of the transgranular fracture surfaces is clearly evident.

Fig. 5 shows micrographs for a sample nitrided in nitrogen/5% hydrogen without pretreatment. Fracture is again transgranular but the morphology is more fine grained than that for the samples nitrided after pretreatment.

4. Discussion

The results of Fig. 1 for nitridation following pre-

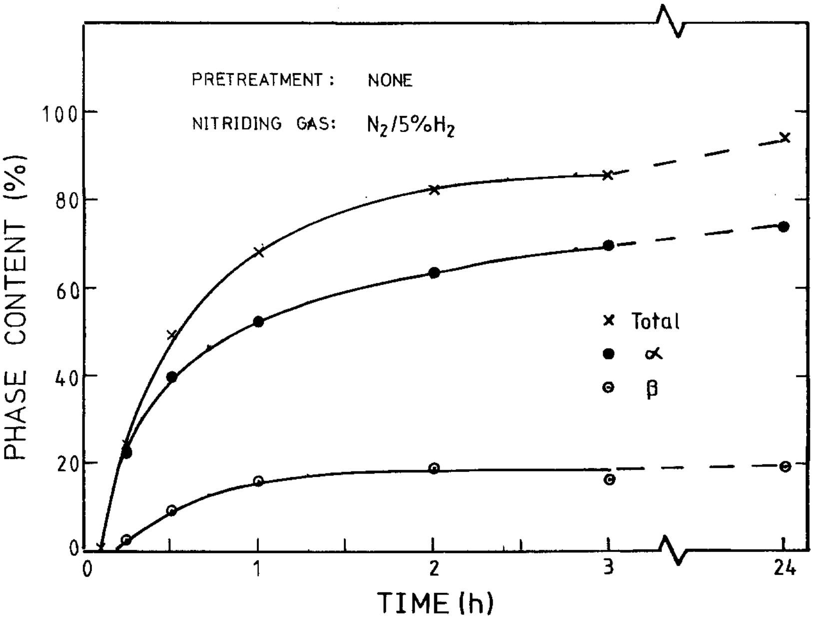

Figure 3 α- and β-silicon nitride phase contents plotted against time for samples nitrided in nitrogen/5% hydrogen without pretreatment.

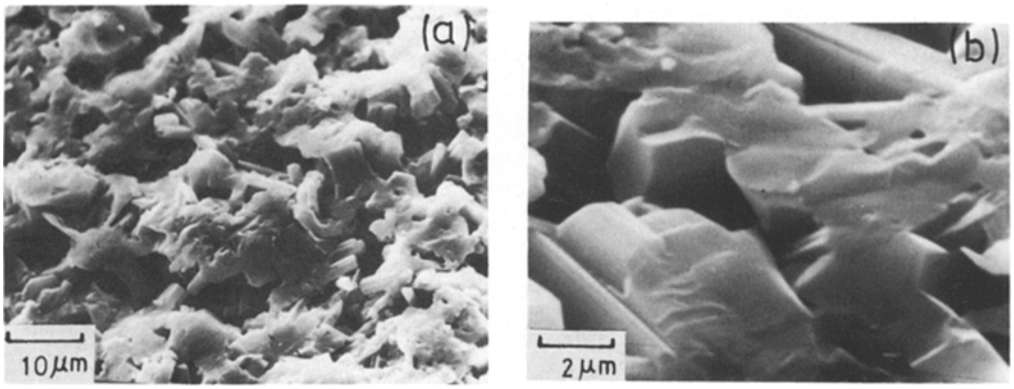

Figure 4 Scanning electron micrographs of the fracture surface of sample pretreated in hydrogen for 1 h, then nitrided in nitrogen/5% hydrogen (98% nitridation).

treatment show three regimes as discussed elsewhere [1]. The kinetics of the first stage are linear. The reaction rate decreases continuously in the second stage and in nitrogen and nitrogen/5% hydrogen, ends abruptly after ~ 1 h giving a third stage of zero reaction rate. At the end of the second stage the samples are almost fully nitrided (~ 2% unreacted silicon).

The results show that high-purity silicon powder of suitable particle size can be rapidly nitrided to almost complete conversion in nitrogen or nitrogen/5% hydrogen at atmospheric pressure following pretreatment to remove the native silica layer.

Two observations are of special significance for the commercial production of RBSN and might readily be incorporated into existing procedures. These are (a) the effectiveness of the argon pretreatment and (b) the reaction rate can be controlled by controlling the nitrogen content of the nitriding gas. A mixture of nitrogen and an inert gas (for example argon), instead of nitrogen and hydrogen, can be used to control the nitrogen content of the nitriding gas.

A comparison of the results of Fig. 1, for nitridation with and without pretreatment, clearly shows the retarding effect of the silica layer on the nitridation kinetics of high-purity silicon powder. Without the pretreatment stage, the silicon powder was nitrided in nitrogen to only ~ 30% conversion after 24 h.

Fig. 2 shows that α- and β-nitride are formed together, the α-nitride forming at the much faster rate. Fig. 3 shows that the formation of β-nitride stops after ~ 1.5 h (~ 20% β), the further conversion at longer times being due to the formation of α-nitride. This is in agreement with previous work [9].

The nearly constant α/β nitride contents (~ 81% α, 17% β) and the indistinguishable growth morphologies, typified by Fig. 4, irrespective of the nitriding gas composition following pretreatment, are strongly supportive of the view that,

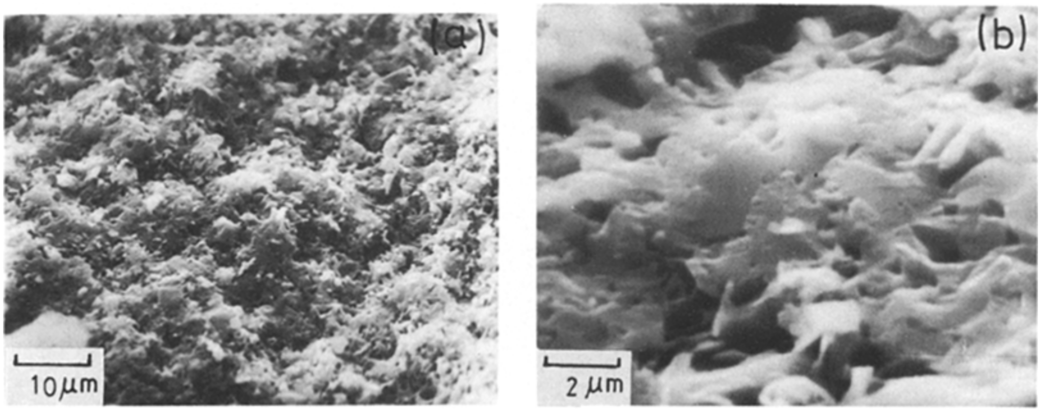

Figure 5 Scanning electron micrographs of the fracture surface of sample nitrided in nitrogen/5% hydrogen without pretreatment (95% nitridation).

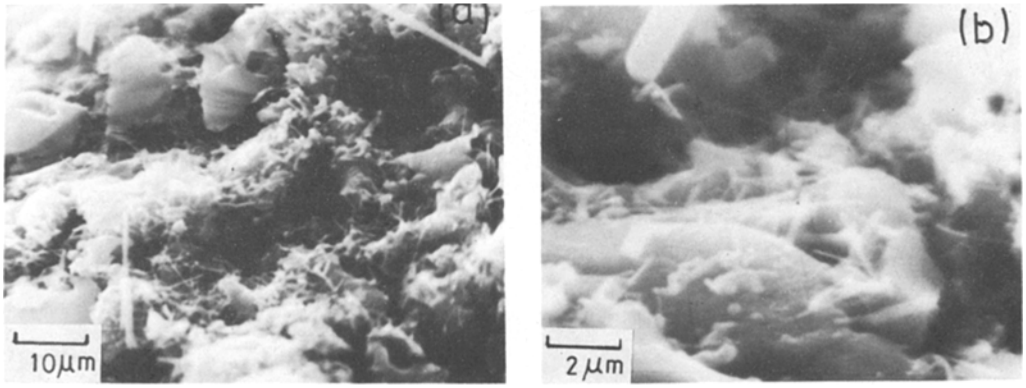

Figure 6 Scanning electron micrograph of the fracture surface of sample nitrided in nitrogen/5% hydrogen (without pretreatment) for 0.25 h (23% nitridation).

once the silica layer has been removed the reaction occurs between nitrogen and silicon vapour, these being the gas-phase constituents common to all cases. It is believed that α-nitride is formed by the reaction between silicon vapour and nitrogen while β-nitride is formed by the nitridation of the silicon surface [1]. The morphology of the fracture surfaces is readily reconciled with this hypothesis for the formation of the α-nitride.

The α/β nitride contents (75% α, 20% β) obtained from nitridation in nitrogen/5% hydrogen without the pretreatment stage are not very different from the values for nitridation following pretreatment and so it would seem that the dominant mechanism for nitridation in nitrogen/5% hydrogen without pretreatment is again as outlined above. The fine-grained nature of the micrographs shown in Fig. 5 might be attributed to the role of the silica layer in the early stages when nitridation of the silica by the SiO_2/N_2 reaction is thought to be significant [1]. Fig. 6 shows a scanning electron migrograph of a sample nitrided in nitrogen/5% hydrogen without pretreatment, for 0.25 h; a number of fine whiskers are clearly seen.

The differences in microstructure of RBSN formed by nitridation with and without pretreatment may be important in determining subsequent densification behaviour. The RBSN formed by nitridation in nitrogen/5% hydrogen without pretreatment has a finer grain structure and under similar sintering conditions should densify faster than the coarse-grained RBSN formed by nitridation following pretreatment.

5. Conclusions

The results show that high-purity silicon powder can be rapidly nitrided to nearly complete conversion in gases at atmospheric pressure, following pretreatments designed to remove the native silica layer on the silicon particles.

Argon gas containing a very low oxygen content has been found to be an effective agent in the removal of the silica layer. The rate of nitridation can be controlled by controlling the nitrogen content of the nitriding gas.

For nitridation following pretreatment, the observations suggest a mechanism involving the chemical vapour deposition of massive silicon nitride by the reaction of silicon vapour with nitrogen gas.

Acknowledgement

Support by the Science and Engineering Research Council through a Research Grant is acknowledged.

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Received 4 February and accepted 12 May 1983