Intrinsic Nitridation Kinetics of High-Purity Silicon Powder

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The intrinsic nitridation kinetics of high-purity silicon solid to form silicon nitride were determined by thermogravimetric analysis technique. The initial rate method was used to avoid kinetics falsification due to intraparticle diffusion limitation caused by the formation of silicon nitride layer around the silicon particles. Relatively small sample sizes were used to eliminate the interparticle diffusion limitation (compact effect) that becomes important as the reaction proceeds, owing to the expansion of the individual particles and filling of the initial pores within the compact. The effect of hydrogen addition to the nitriding gas, as well as the influence of the flow rate, on the reaction progress was also investigated.

Introduction

Silicon nitride is an important ceramic material with properties including good mechanical strength maintained to high temperatures, high resistance to corrosion, and low thermal expansion coefficient which reduces the risk of thermally induced failure. Reaction bonding is an attractive method to synthesize silicon nitride by direct nitridation of silicon powder at temperatures below its melting point (1,414°C). This process yields a product with the same external dimensions, with much less porosity, as compared to the silicon preform.

Although many studies related to the kinetics of solid silicon nitridation to form silicon nitride (reaction-bonding process) have been published in the literature, most of them have failed to isolate intrinsic reaction behavior from global or compact effects. The latter effects arise from several sources. The first is that the local nitrogen concentration in the compact is lower than the bulk value owing to interparticle diffusional gradient. Secondly, this gradient is progressively enhanced during reaction owing to the 21.6% volume expansion of silicon particles as they form silicon nitride. Finally, intraparticle diffusion is ineluctable because of the silicon nitride layer that forms around the Si particle and presents a barrier for nitrogen diffusion (Atkinson et al., 1974; Moulson, 1979). In addition, impurities in the silicon itself or in the nitriding atmosphere originating from the nitriding gas or the furnace tube can also significantly influence the course of the nitridation reaction. Failure to properly account for any of the aforementioned effects can lead to erroneous reaction kinetics.

We have recently discussed these issues and determined the intrinsic nitridation kinetics of pure (99.999%) silicon by using small sample sizes of well-defined surface areas, and by using the "initial reaction rate" technique (Pigeon and Varma, 1993). However, the kinetics were determined only as a function of temperature and the surface area of solid silicon, while maintaining nitrogen concentration in the nitriding gas as constant. In the present work, by conducting experiments under different nitrogen concentrations in the presence of hydrogen (whose importance is discussed below), we determine the intrinsic nitridation kinetics of high purity silicon also as a function of nitrogen concentration (partial pressure). These kinetics can be used to develop a fundamental model of the reaction-bonded silicon nitride (RBSN) process that includes diffusion of nitrogen within the compact, as well as through the growing silicon nitride layer on individual silicon particles. In addition, we discuss some factors that affect the course of the reaction-bonding process.

Role of Hydrogen

Hydrogen plays an important role in removing the native silica layer (~ 3 nm thick) that covers the external surface of the silicon particles. It is well established that this silica layer has a retarding effect on nitridation kinetics, and that pretreatment of the powder with hydrogen accelerates its removal, and thus enhances the reaction rate (Dervisbegovic

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and Riley, 1981; Rahaman and Moulson, 1984). Hydrogen is also believed to discourage the formation of atomic nitrogen, and hence is a factor in slowing down nitrogen diffusion through solid Si_3N_4 matrix and liquid phase, both associated with β-Si_3N_4 production (Jennings, 1983). In fact, Lindley et al. (1979) found that the α/β ratio increases as the hydrogen content in the nitriding gas increases. It was also observed that the addition of hydrogen to the reaction mixture aids in the formation of a finer and more uniform microstructure, as compared to pure nitrogen (Mangels, 1981; Rahaman and Moulson, 1984; Kim and Kim, 1985; Ziegler et al., 1987), and that the strength of the final product increases with the α/β ratio (Moulson, 1979). In general, addition of $\sim 5\%$ hydrogen enhances remarkably the overall kinetics of the reaction and increases the α/β ratio (Lindley et al., 1979; Mangels, 1981; Rahaman and Moulson, 1984). From 5 up to 10% H_2, there is only a slight enhancement in the reaction rate, while above 10% the rate falls due to the nitrogen diluent effect (Dervisbegovic and Riley, 1981).

It is worth noting that α-Si_3N_4 and β-Si_3N_4 are the two crystalline forms of silicon nitride. The α phase is formed predominantly below the melting point of Si, while the β phase is favored at higher temperatures. Both α and β phases have a hexagonal form, but different lattice parameters. More details regarding the structure of the two phases can be found elsewhere (Forgeng and Decker, 1958; Ruddlesden and Popper, 1958; Thompson and Pratt, 1967; Ziegler et al., 1987). Most workers agree that a part of α-Si_3N_4 is formed in the gas phase via a reaction mechanism between molecular nitrogen and silicon monoxide, and that hydrogen contributes favorably to this process (Lindley et al., 1979; Dervisbegovic and Riley, 1981). Indeed, increases in the SiO signal in the gas phase have been observed by mass spectroscopy, when silicon with a surface of oxide layer was heated in N_2/H_2 mixture as compared to pure nitrogen (Lin, 1975; Lindley et al., 1979).

The possible reactions involved in the formation of SiO are as follows (Moulson, 1979; Lindley et al., 1979; Dervisbegovic and Riley, 1981; Jennings, 1983)

$$SiO_2(s) + Si(s) \leftrightarrow 2SiO(g) \quad \Delta G(1{,}350°C) = 147\ \text{kJ/mol} \qquad (1)$$

while under reduced oxygen partial pressure, silica is reduced following

$$SiO_2(s) \leftrightarrow SiO(g) + 1/2O_2(g) \quad \Delta G(1{,}370°C) = 382\ \text{kJ/mol} \qquad (2)$$

In the presence of hydrogen, reduction of the silica layer

$$SiO_2(s) + H_2(g) \leftrightarrow H_2O(g) + SiO(g) \quad \Delta G(1{,}350°C) = 230\ \text{kJ/mol} \qquad (3)$$

can occur and oxygen can recombine with hydrogen to form water vapor

$$H_2(g) + 1/2O_2(g) \leftrightarrow H_2O(g) \quad \Delta G(1{,}350°C) = -314\ \text{kJ/mol} \qquad (4)$$

H_2O generated from reactions 3 and 4 may react with silicon according to

$$H_2O(g) + Si(s) \leftrightarrow SiO(g) + H_2(g) \quad \Delta G(1{,}350°C) = -84\ \text{kJ/mol} \qquad (5)$$

In the absence of hydrogen, active oxidation of silicon can take place

$$Si(s) + 1/2O_2(g) \leftrightarrow SiO(g) \quad \Delta G(1{,}350°C) = -477\ \text{kJ/mol} \qquad (6)$$

A detailed discussion of the feasibility of the above reactions under different nitriding conditions is given by Moulson (1979) and by Pigeon et al. (1993). The SiO formed from the different possible reactions (1, 2, 3, 5, 6) can react with nitrogen to form silicon nitride

$$3SiO(g) + 2N_2(g) \leftrightarrow Si_3N_4(g) + 3/2O_2(g) \quad \Delta G(1{,}350°C) = 502\ \text{kJ/mol} \qquad (7)$$

Although ΔG for reaction 7 is positive and large, it is generally accepted that it is feasible when the partial pressure of oxygen is low ($\sim 10^{-16} - 10^{-19}$ atm) in the presence of hydrogen (Moulson, 1979; Lindley et al., 1979; Pigeon et al., 1993), and is also feasible but to a lesser extent in the absence of hydrogen (Lindley et al., 1979). It is even considered to be the major contributor towards the formation of the alpha phase through a CVD-like process (Moulson, 1979; Rahaman and Moulson, 1984; Jennings, 1983), by reaction between adsorbed SiO and N_2 at a silicon nitride surface (Dervisbegovic and Riley, 1981), or by a vapor-liquid-solid (VLS) mechanism if impurities (such as Fe) that can locally lower the melting point of Si are present (Messier and Wong, 1973; Jennings and Richman, 1976; Moulson, 1979).

Experimental Procedure

Experimental apparatus

The experimental apparatus used is shown in Figure 1. Essentially, the apparatus can be divided into three sections: a gas mixing section, the reactor section, and the analytical section. The gas mixing section allowed the delivery of the gas mixture at the desired composition to the reactor section following its passage through a static mixer and an oxygen/water trap (Oxiclear gas purifier, Alltech Associates, Inc., Deerfield, IL) to lower concentrations to 5×10^{-8} atm (50 ppb). The reaction section consisted mainly of a Cahn 2000 thermogravimetric recording electrobalance with a sensitivity of 0.5 μg and a maximum capacity of 1.5 g, along with a rapid heat/cool, Kanthal Super 33 split-shell furnace (Model 3320, Applied Test Systems, Inc., Butler, PA) controlled by a Pt-Pt 10% Rh thermocouple placed directly below the sample. The electrobalance was enclosed in a gas-tight vacuum vessel to allow strict control of the nitriding atmosphere. The reactor consisted of a 3/4-in.-ID (19-mm-ID) high-purity alumina tube (McDanel Refractory Co., Beaver Falls, PA) lined with a 0.025-in.-thick (0.6-mm-thick) sheet of molybdenum (99.95%)

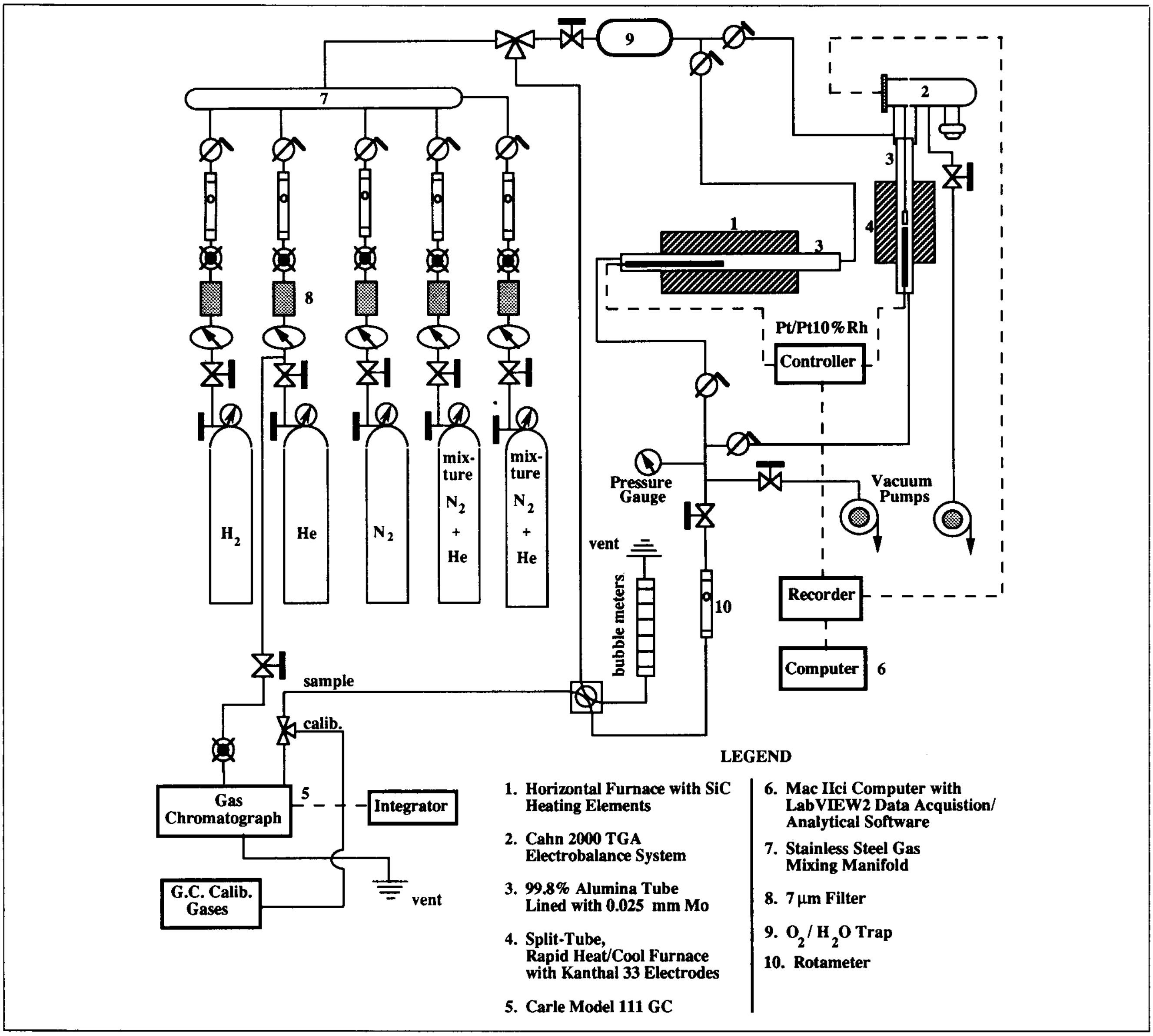

Figure 1. Experimental setup for silicon nitridation.

rolled into the shape of a cylinder covering the inner wall to "getter" any residual oxygen left in the system prior to nitridation or any oxygen or other impurities released by the tube itself. The final section of the experimental apparatus involved a Carle 111 gas chromatograph and an integrator for monitoring the feed and exit stream compositions.

Procedure

For each experiment, a sample of free silicon powder (99.999% purity, Cerac, Inc., Milwaukee, WI) was weighed into a small cylindrical Mo crucible (6 mm diameter), supported in a tungsten basket and attached to a single-crystal sapphire hangdown wire. To minimize the experimental error and obtain reproducible results, different samples with narrow size-distribution and well-defined surface areas were used (see Table 1). The experiments were conducted at 1 atm total pressure, and the UHP reacting gas consisted typically of 5% H_2 in a N_2-He mixture, where the He was used as a diluent to obtain the desired N_2 composition. This mixture was admitted to the reactor only after extensive outgassing of the system had been carried out to minimize the presence of impurities in the system (oxygen < 1 ppm). The outgassing procedure consisted of pumping down the system to approximately 0.1 torr and filling it with the UHP reaction gas mixture (H_2-N_2-He) at least four times, and then the reaction mixture was allowed to flow through the apparatus for several hours at a typical flow rate of 150 ± 2 cm^3/min. The furnace was heated at maximum controller output from room

Table 1. Characteristics of Silicon Samples Used

Particle Size (μm)	5–10	10–15	15–20
BET Area (m^2/g)*	1.02	0.73	0.58

*Determined by nitrogen adsorption using a Quantasorb apparatus (Quantachrome Corporation).

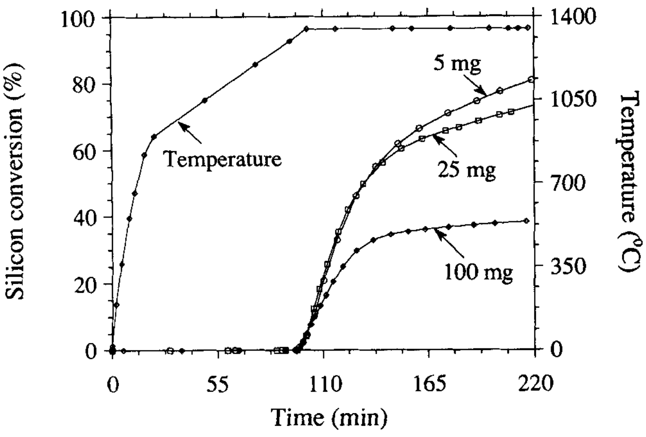

Figure 2. Effect of sample size on silicon nitridation kinetics.

Si particle size = 5–10 μm; gas composition = 95% N_2, 5% H_2; T = 1,350°C. The temperature, measured just below the sample, is also shown as a function of time.

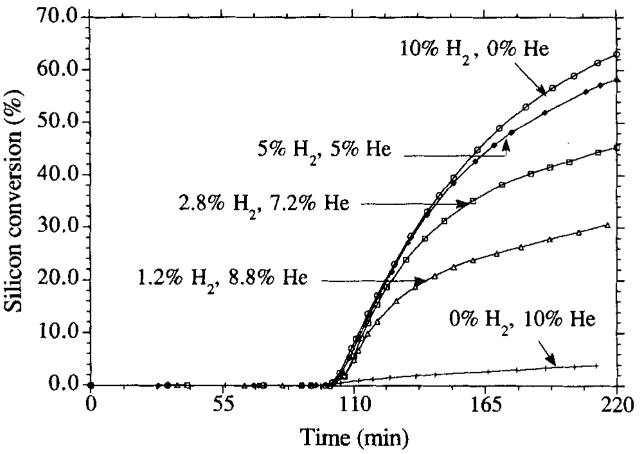

Figure 3. Effect of H_2 addition to the nitriding gas on reaction behavior.

Si particle size = 5–10 μm; gas composition = 90% N_2, H_2-He 10%; T = 1,350°C.

temperature to 900°C, followed by a linear ramp at a rate of 340°C/h up to the desired isothermal reaction temperature, as shown in Figure 2. The electrobalance was connected to a strip-chart recorder yielding the continuous evolution of the nitridation reaction. In the data that follows, time zero for the experiments was taken as the instant when heating of the furnace was initiated. Additional details about the experimental procedure are available elsewhere (Maalmi, 1996).

Results and Discussion

A series of experiments were conducted to determine the appropriate sample size for determining the kinetic parameters following the "initial rate" technique. As can be seen from Figure 2 and as discussed elsewhere (Pigeon and Varma, 1993), the process of nitridation can be divided into three stages: In the first stage (up to 5–6% conversion), the reaction is relatively slow due to either devitrification of the silica layer or initial nucleation. In the second stage, the reaction rate is higher, and essentially constant, leading to an almost linear increase in conversion with time (for subsequent analysis, the highest rate during this stage is referred to as the "initial rate"). In the third stage, the reaction slows down owing to diffusional limitations of nitrogen in the growing product layer (intraparticle) as well as in the compact (interparticle) because of the decrease in porosity, rendering full conversion difficult for large compacts. The results for silicon conversion shown in Figure 2 indicate that the "initial reaction rate" is the same when increasing the sample size from 5 mg to 25 mg, but it is lower for a sample of size 100 mg. Hence, samples of size up to 25 mg may be considered free from compact effects (that is, interparticle diffusion limitation) from the viewpoint of the "initial rate." Thus, to minimize the relative experimental error, samples of size ~ 25 mg were used instead of 5 mg, since sample weights were determined with an error of ±0.1 mg.

Figure 3 shows the effect of hydrogen addition to the nitriding gas on silicon conversion for fixed nitrogen composition (90%) and temperature. It is readily seen that there is virtually no reaction in the absence of hydrogen, and that the reaction rate increases with hydrogen content. It can also be seen that the "initial rate" remains essentially the same beyond about 2.8% H_2, although the overall conversion may increase substantially. From 5 to 10% H_2, the increase in the overall conversion is also relatively small, as discussed earlier. For determination of the intrinsic kinetics and the remaining experiments, a 5% H_2 concentration was maintained.

Figures 4 and 5 show the influence of the nitriding gas composition on silicon conversion for samples of particle sizes 5–10 μm and 10–15 μm, respectively. Similar data were obtained for other particle sizes and reaction temperatures. A linear regression analysis of the "initial rate" data (Figure 6) showed that the reaction order with respect to nitrogen concentration is close to unity (0.92±0.07), and is independent of particle size and temperature. This first-order dependence suggests a proportional variation of the reaction rate with the amount of nitrogen adsorbed on the Si surface.

Figures 7a and 7b show the conversion evolution as a function of temperature for two different gas compositions (95% N_2-5% H_2 and 47.5% N_2-47.5% He-5% H_2) for silicon samples of 5–10 μm particle size. A linear regression analysis of

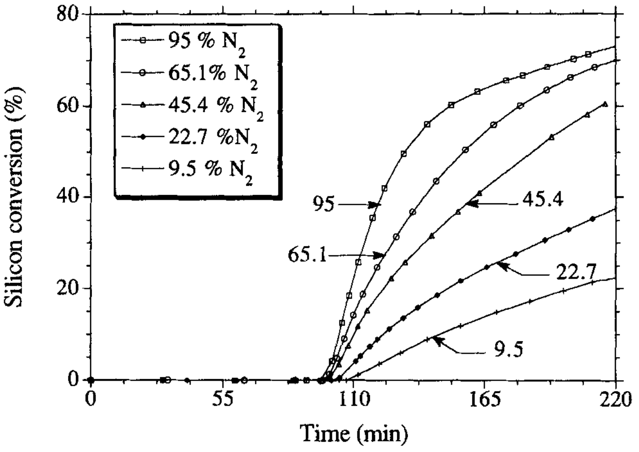

Figure 4. Effect of gas composition on the nitridation behavior.

Si particle size = 5–10 μm; T = 1,350°C.

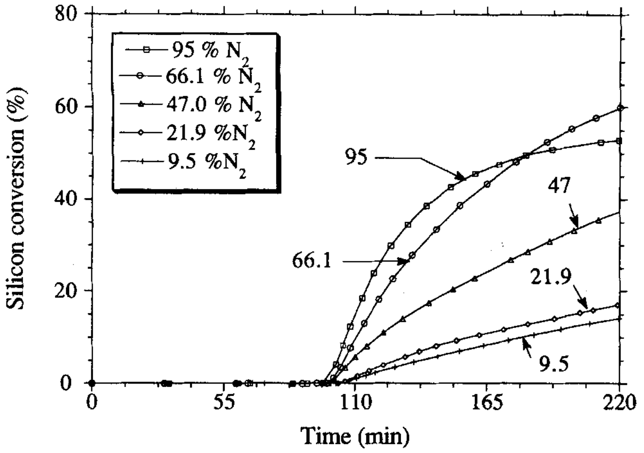

Figure 5. Effect of gas composition on the nitridation behavior.

Si particle size = 10–15 μm; T = 1,350°C.

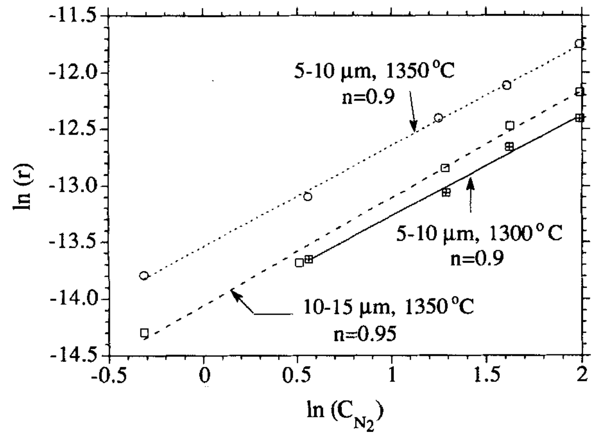

Figure 6. Linear regression analysis of the initial rate data to determine the reaction order (n) with respect to nitrogen.

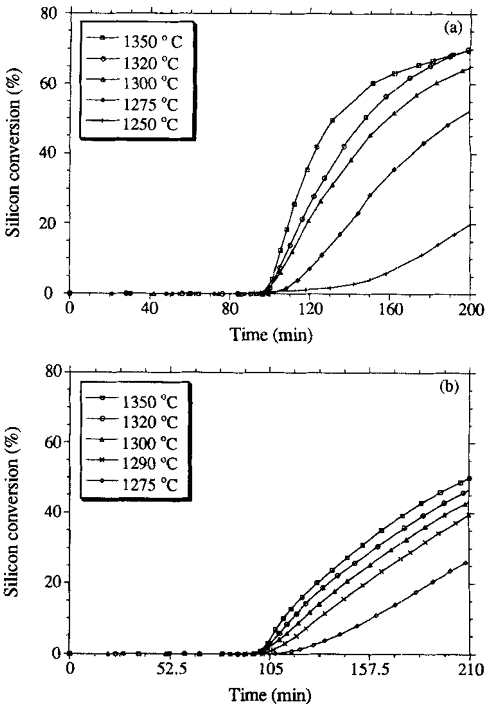

Figure 7. Effect of temperature on the nitridation kinetics.

Si particle size = 5–10 μm. (a) Gas composition = 95% N_2, 5% H_2; (b) gas composition = 47.5% N_2, 47.5% He, 5% H_2.

the "initial rate" data (Figure 8) shows that the activation energy is not affected by the gas composition. Thus, He addition to the nitriding gas has no effect on the intrinsic kinetic behavior, although it has been shown to influence the reaction-bonding process (Kim and Kim, 1984). The average activation energy is 317 ± 10 kJ/mol, which compares well with the value 301 kJ/mol reported recently (Pigeon and Varma, 1993), where it was also shown that this corresponds to diffusion control of N_2 through the silicon nitride product layer. It should be noted here that the intraparticle or internal diffusion in noncatalytic gas-solid reactions is somewhat different from that in catalytic systems. Owing to the nature of noncatalytic reactions such as the one under study, diffusion of gas or volatilized solid reactant through nuclei or early solid product is inevitable, and is a part of the reaction mechanism. In the previous work by Pigeon and Varma (1993), the reaction order relative to the surface area of silicon powder was determined to be 0.84, a value close to one, which is generally assumed for noncatalytic gas-solid reactions and means simply that the "initial reaction rate" is proportional to the available surface area. Combining this with the results obtained above, the intrinsic kinetics of the nitridation reaction of high purity silicon below its melting point is given by the expression

$$r = 2.5\cdot 10^4 \exp\left[\frac{-317\ (\text{kJ/mol})}{\text{RT}}\right] \times (C_{N_2})^{0.92}(S_a)^{0.84}\ \text{mol Si/g Si-s} \qquad (8)$$

where C_{N_2} is nitrogen concentration (mol/m^3) and S_a is Si-specific surface area (m^2/g). It is worth emphasizing that although the reaction mechanism of silicon nitridation is complex as discussed earlier, an overall expression such as Eq. 8 can be useful in developing a model to describe the

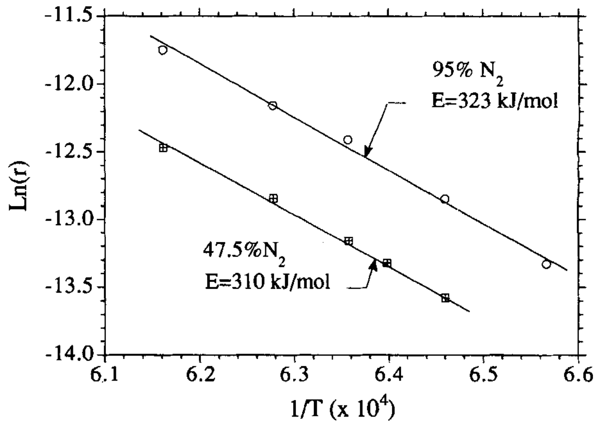

Figure 8. Linear regression analysis of the initial rate data to determine the activation energy (E).

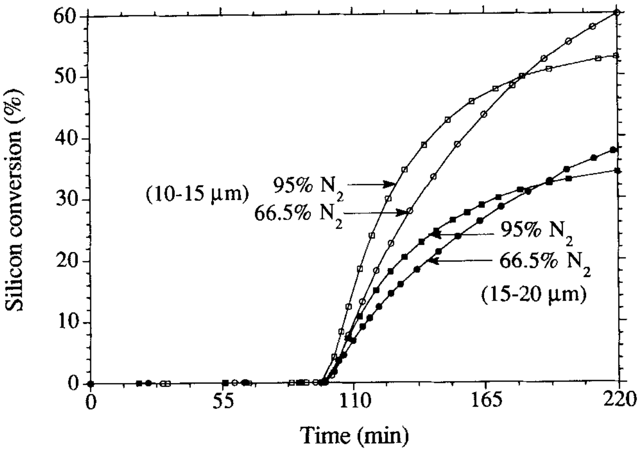

Figure 9. Effect of nitriding gas composition on silicon conversion (crossover behavior).

$T = 1,350°C$.

reaction-bonding process, which includes inter- and intraparticle diffusion, as well as reaction.

In Figure 5, an unusual cross-over between the curves of conversion vs. time corresponding to nitriding gas compositions of 95% N_2 and 66.1% N_2 may be seen. Other experiments were conducted using different particle sizes, and the same features were observed as shown in Figure 9. This cross-over behavior has been observed previously (Atkinson et al., 1976) and can be interpreted as follows. When the compact reacts at high "initial rate" (high N_2 concentration), the silicon particles at the outer layer of the compact react faster, leading to less porosity available for N_2 diffusion into the inner part of the compact. Thus, the reaction is slowed down and the characteristic "kneeing" in the conversion occurs early. On the other hand, when the "initial rate" is low (at lower N_2 concentration), clogging of the pores at the external surface is less acute, and the reaction continues more uniformly in the compact. This can be better seen from the SEM micrographs of Figure 10 that show the top surface of two identical compacts reacted under different nitriding gas compositions. It may be seen that in Figure 10a (higher N_2 concentration), the structure is fibrous, which is an indication of high degree of conversion, and the pore sizes are small. For the case of lower N_2 concentration (Figure 10b), the texture is coarser, the particles have reacted less, and there are more pores available for N_2 diffusion, although the overall conversion is higher for the sample in Figure 10b than that in Figure 10a.

Figure 11 shows the effect of nitriding gas-flow rate on the reaction behavior. It can be seen that the "initial reaction rate" is not affected by the flow rate, but the reaction starts slowing down early as the flow rate increases. Some workers (Jennings and Richman, 1976; Lindley et al., 1979) have suggested that this could be attributed to the fact that at high flow rates volatilized silicon and other gases can be swept away by the nitriding gas, reducing the formation of a part of α-Si_3N_4 that is normally formed in the gas phase. Jennings and Richman (1976) and others (Jones and Lindley, 1976; Lindley et al., 1979; Jennings et al., 1988) carried out experiments in flowing and stagnant (or very small flow rate) gas, and found an inverse correlation between the gas-flow rate and the α/β ratio. Other workers suggest that in flowing conditions impurities such as oxygen are introduced to the system (Jennings, 1983) or the gas composition in the system is modified (Jennings et al., 1988), which influence the course of the reaction.

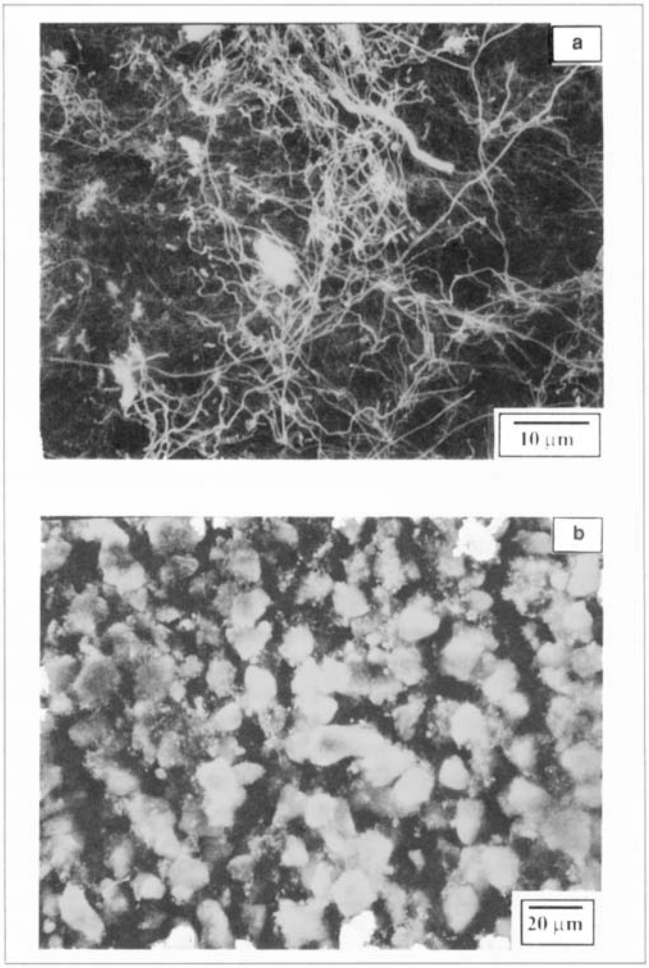

Figure 10. SEM micrographs of the top surface of partially reacted silicon compacts.

Si particle size = 10–15 μm; $T = 1,350°C$. (a) Gas composition = 95% N_2, 5% H_2; (b) gas composition = 66.5% N_2, 28.5% He, 5% H_2.

If we assume that the volatilized silicon in the form of SiO is swept away by the nitriding gas in flowing conditions, then a non-negligible part of the initial silicon would simply be lost during reaction (because of the large difference in conversions observed in Figure 11). However, we did not notice any weight loss under reaction conditions during the thermogravimetric analysis (TGA) recordings. One can argue that the SiO loss is not noticeable because of the higher increase in weight due to other mechanisms that contribute to the formation of both α and β phases. If this were true, the actual conversion would be higher than that obtained by the TGA system since the unreacted silicon in the final product would be less than expected. The X-ray diffraction (XRD) analysis results of the products obtained with different flow rates, shown in Table 2, were obtained using the method described by Gazzara and Messier (1977) for the unreacted silicon (hence, the overall conversion), and by Pigeon and Varma (1992) for the α/β phase ratio. These results show that the

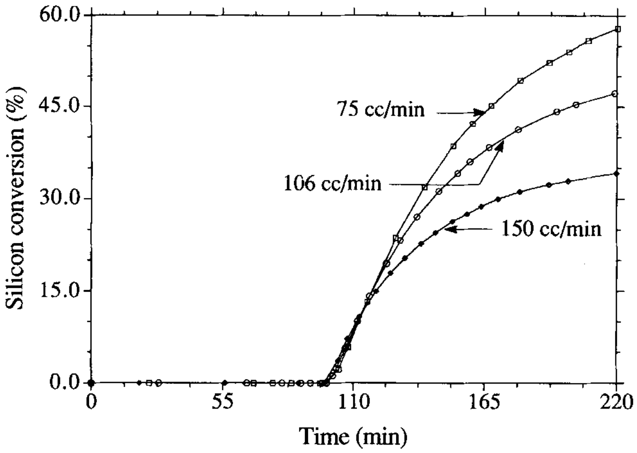

Figure 11. Effect of nitriding gas-flow rate on silicon conversion.

Si particle size = 15–20 μm; gas composition = 95% N_2, 5% H_2; T = 1,350°C.

conversions obtained by the two methods (XRD and TGA; errors for both less than 2%) are the same, which refute the idea that at high flow rates, SiO is swept away by the flowing gas. A slight loss of silicon (1–2%) in the form of SiO at high flow rates is possible, but a loss of 25% or more (see Figure 11) is very unlikely. The interpretation of the decrease in conversion and the α/β ratio with increase in the flow rate lies most probably in the fact that at higher flow rates, impurities such as oxygen are introduced in the system which prevent reaction (Eq. 7) from occurring. At lower flow rates or stagnant gas conditions, impurities (such as oxygen) that are initially present are consumed by the different possible reactions described above (that is, reactions 4 or 6), which create zones within the sample with very low P_{O_2} that allow the formation of α-Si_3N_4 via reaction 7.

Conclusions

It was shown in this work that the intrinsic kinetics of the nitridation reaction of high purity solid silicon in the temperature range 1,250–1,350°C has almost a first-order dependence on the nitrogen concentration. Small sample sizes (~ 25 mg of free powder) were used to eliminate the compact effect (that is, interparticle diffusion) on the reaction rate, and the "initial rate" technique was used to avoid intraparticle diffusion limitation. It was also shown that by clogging the external pores of the compact which are required for nitrogen diffusion, a high "initial rate" can have a deleterious effect on the reaction-bonding process. Finally, it was shown that lower conversions obtained under high flow rate conditions are most likely due to the introduction of trace impurities along with the nitriding gas, and not due to the sweeping of volatile silicon monoxide.

Table 2. Silicon Conversion and α/β Phase Ratio for Samples Reacted Under Different Nitriding Gas Flow Rates*

Flow Rate (cm^3/min)	TGA Conversion	XRD Conversion	α/β Ratio
150	34.0	32	14.8
106	48.4	48	16.9
75	59.0	60	22.4

*T = 1,350°C; Si particle size = 15–20 μm; gas composition = 95% N_2, 5% H_2.

Acknowledgments

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