JOURNAL OF MATERIALS SCIENCE 18 (1983) 951–967

Review
On reactions between silicon and nitrogen
Part 1 *Mechanisms*

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An attempt is made to rationalize various reaction mechanisms for the formation of Si_3N_4 from gaseous nitrogen and solid silicon. It is suggested that a fundamental difference between α- and β-Si_3N_4 is that the former results from silicon complexing with molecular nitrogen and the latter results from complexing with essentially atomic nitrogen. Well established mechanisms (as well as controversial ones) are analysed in the light of this difference and are shown to be operative under various reaction conditions. The influence of some common reaction variables are interpreted with respect to their influence on either silicon or nitrogen or both.

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1. Introduction
The reaction between silicon and nitrogen has been extensively studied and recent reviews [1, 2] have summarized and refined a large body of information. Ideas concerning the formation mechanisms of the two product phases, α- and β-Si_3N_4 in their various morphologies are of much interest because it is through control of these reactions that improvements in microstructure can be achieved.

Some aspects of the reactions are becoming generally accepted but because of the complexity of the system, particularly when considering the role of impurities in both nitrogen and silicon, full details of all the reactions are still lacking. This paper suggests a framework for viewing the reactions which may help to further understand the mechanisms. It is based largely on a thermodynamic analysis of the reaction process and this leads to the idea that it is worth considering the reactivity of the nitrogen molecule. It is not intended that this paper answer all questions, the intention is to motivate experiments and discussion which can improve understanding and help control the formation of silicon nitride.

2. Formation and structure of silicon nitride
2.1. Brief background
Typical nitriding schedules involve heating silicon, usually a powder compact, and nitrogen to temperatures between 1300 and 1500° C and often the temperature is kept in the lower region for some hours before it is raised to a higher level. Both α- and β-Si_3N_4 phases are almost always formed but it is generally observed that α-Si_3N_4 forms preferentially in the early stages and at lower temperatures. Furthermore, impurities which cause the volatization and subsequent reaction of silicon, for example the formation of SiO followed by reduction in $N_2 + H_2$ mixtures [1, 3–5] may encourage the formation of α-Si_3N_4 while impurities such as iron [1, 6–8] in silicon, which lowers melting temperature, encourages the formation of β-Si_3N_4. The reaction can proceed only after any surface oxide is removed and this may be an important accelerating role of hydrogen [9] and iron [10, 11]. A marked difference in product formed in static as opposed to a flowing nitrogen atmosphere [3–5, 12] is thought to be related to the transport of impurities either to or from the

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reaction site [3–5, 9]. Most consideration in the literature has been given to how impurities may affect silicon.

Both the α- and β-Si_3N_4 phases are hexagonal and their detailed structure have been adequately discussed elsewhere [13–21]. Silicon is tetrahedrally coordinated, nitrogen has trigonal planar coordination, a configuration which is somewhat unusual. Furthermore, the Si–N bond length is most often shorter than would be expected from simple covalent bonding [21]. Like $N(SiH_3)_3$ [22] these latter two facts can be explained [21] by invoking various degrees of dπ–pπ bonding which appears to be energetically favoured in the Si–N bond. The α-Si_3N_4 phase exhibits some longer bonds, however, which can be explained [21] by noting that the relative orientations of certain silicon to nitrogen atoms forbid much dπ–pπ bonding. Indeed the α-Si_3N_4 structure is more strained [23] than the β-Si_3N_4 structure which probably implies that it forms under more constrained or sterically hindered conditions.

The less strained β-Si_3N_4 phase may have a slightly lower Gibbs free energy than α-Si_3N_4 but because of large error bars on experimental measurements [24–29] it has only been demonstrated that the values for the two phases are close to one another. Moulson [1] derived the following equations for the free energy of reaction, firstly using data of Pehlke and Elliott [25], whose results are similar to those from Blegen [28], and Hincke and Brantley [24], where both α- and β-Si_3N_4 phases formed at temperatures between 1400 and 1700° C, to obtain Equation 2. Then, using the heat of fusion from Olette [30], he derived Equation 1, and heat of vaporization of Grieveson and Alcock [31], derived Equation 3. Reactions 1 and 3 apply only to temperatures near the melting point of silicon. The reactions are always somewhat exothermic:

$$3Si(s) + 2N_2(g) = Si_3N_4(s)$$

$$\Delta G = -723 + 0.315T \text{ kJ mol}^{-1} \qquad (1)$$

$$3Si(l) + 2N_2(g) = Si_3N_4(s)$$

$$\Delta G = -874 + 0.405T \text{ kJ mol}^{-1} \qquad (2)$$

$$3Si(g) + 2N_2(g) = Si_3N_4(s)$$

$$\Delta G = -2080 + 0.757T \text{ kJ mol}^{-1} \qquad (3)$$

β-Si_3N_4 is found in greater abundance [12, 32–34] when reactions are carried out at higher temperatures. Along with some structural evidence [35] it has been argued that β-Si_3N_4 is a high temperature phase and α-Si_3N_4, therefore, is a low temperature phase. This may be in conflict with free energy and density arguments. (High temperature phase is usually less dense.) Furthermore, α → β-Si_3N_4 transformations have been observed when a liquid is present [7, 20, 35–40], whereas the β → α-Si_3N_4 transformation has never been observed. Certainly the activation energy separating the two phases is large, the transformation is reconstructive [23, 41] involving the breaking and remaking of strong Si–N bonds. Coupled with experimental observations such as the kinetics of α- and β-Si_3N_4 phase formation, these facts have supported the idea [12, 37] that, in general, the formation of each of the two phases is governed by particular and separate reaction mechanisms. The reactions are slow and easily influenced by many variables. Indeed the rate controlling step may change with time and/or changing environment. The reactions forming α- and β-Si_3N_4 are, at the very least, in kinetic competition. This paper will discuss possible reaction routes and their associated thermodynamics and implied kinetics.

2.2. Established theory of formation: mechanisms and some shortcomings

As summarized by Moulson [1] the reaction mechanisms do appear to be separable. He finally states that "...the major growth of β-Si_3N_4 occurs in the liquid phase and, to a minor extent, as a result of the reaction between solid silicon and nitrogen" and "...the growth of α-Si_3N_4 occurs by vapour-phase reactions". Examination of morphologies and conditions which favour each reaction suggests that there is much experimental evidence in support of these hypotheses.

A great deal of evidence supports the idea that the α-Si_3N_4 phase results from reaction of gases [26, 42]. A detailed understanding, however, of why a strained structure results from a gas reaction, where the reactants have the highest degree of freedom, is lacking. It has been suggested [23] that Si–N complexes have difficulty in adopting the β-Si_3N_4 structure when they are formed in the vapour state. This explanation seems incomplete and will be expanded upon later. Furthermore, N_2 gas is very unreactive and a true gaseous reaction seems unlikely. The energy and heat of dissociation at 25° C is:

$$N_2 \rightarrow 2N \qquad \Delta H = 946.76 \text{ kJ mol}^{-1} \qquad (4)$$

$$\Delta G = 912.46 \text{ kJ mol}^{-1}$$

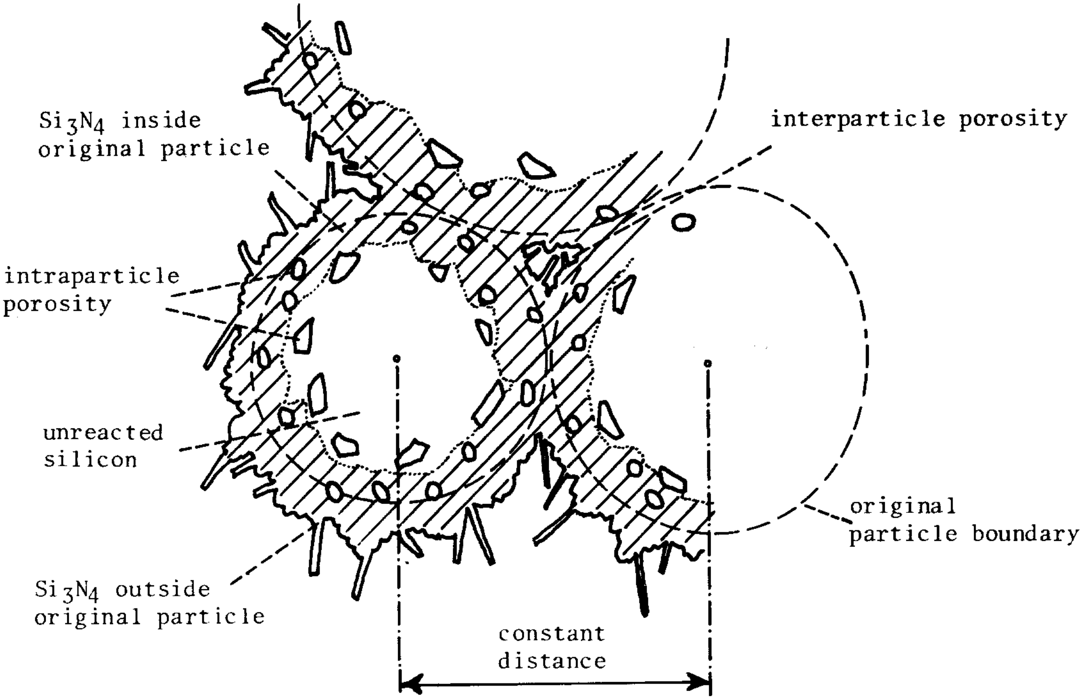

Figure 1 Schematic representation of silicon particles reacting with nitrogen. Porosity both preceeds product as it advances towards the centre of particles and remains entrapped within product. Si_3N_4 also forms in the original void space but the distance between particle centres remains constant indicating that product is not pushed outwards.

It has also been reported [36, 43, 44] that gas phase reactions can lead to β-Si_3N_4. This, of course, presents difficulties and suggests that more detailed reaction conditions must be considered. Possibly the role of impurities, particularly oxygen, may be important. An important observation here is that although the overall reaction rate does not significantly change with the addition of small amounts of oxygen to the nitrogen atmosphere, the α/β-Si_3N_4 ratio is altered [26, 27, 43, 45, 46].

Some observations suggest that reactions which take place on the surface of silicon form β-Si_3N_4 [1, 47]. Early reaction, however, is usually associated with α-Si_3N_4 and, as will be discussed later, some reaction conditions lead to almost 100% α-Si_3N_4 on the surface of silicon.

Further clarification is also necessary of the details of how a reaction with solid silicon might occur. For several reasons a true "solid-state" reaction probably does not take place. In reaction bonded silicon nitride the overall dimensions of the powder compact do not change significantly during the reaction in spite of the fact that the volume of solid increases by 22%. This means that as the reaction continues into a particle, see Fig. 1, solid material is not uniformly pushed outwards, i.e. it only forms in "open" space. Thus reaction into the particle must be be coupled with the creation of space. Silicon, therefore, must be transported out of the particle as a liquid or vapour. (As will be pointed out later, self-diffusion in Si_3N_4 is low and Si_3N_4 does not melt.) Since the kinetics of silicon removal (without melting) and Si_3N_4 growth are not equal the two solids do not stay in contact and a "solid-state" reaction does not take place. If porosity preceeds reaction product then a surface is created on which reaction can take place. After a thin product layer has formed it can thicken only if silicon is transported to the reaction site and therefore it is almost certainly liquid or gas. As new surface is created the process repeats. In addition, it appears [48] that nitrogen does not dissolve in solid silicon, further evidence for excluding a "solid-state" reaction.

The role that liquid silicon may play in the formation of β-Si_3N_4 has been the subject of some research. Very often β-Si_3N_4 is seen as angular "spikes", Fig. 2, which grow from the edge of a grain towards the interior. The reaction site is probably [49, 50] at the end of the spike, thus extending its length in the fast growing *z*-direction.

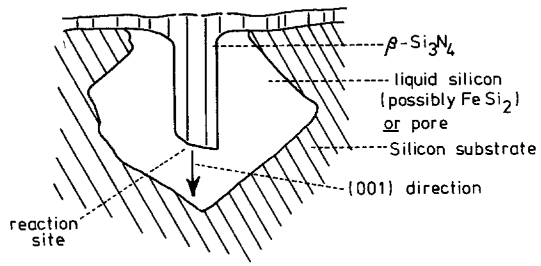

Figure 2 Beta Si_3N_4 growing as a well faceted "spike". It either grows as nitrogen diffuses to the reaction site (fast growing z-direction) through liquid silicon, or it grows into a clean pore as nitrogen slowly diffuses down its length. In the first case the crystal is large and in the second it is small.

A debate has developed around which path the nitrogen takes to the reaction site. Boyer and Moulson [6] have suggested that nitrogen diffuses through a liquid, often $FeSi_2$, and that it is therefore necessary for a liquid to be present. Recent experiments [50] have shown that this mechanism is viable for both pure silicon and silicon with some impurities (iron, titanium and hafnium). Jennings and Richman [12], on the other hand, have proposed the possibility that nitrogen diffuses down the large channels (two types: (a) 0.15 nm and (b) 0.25 nm diameter) which exist in the z-direction of the β-Si_3N_4 structure. Diffusion coefficients and activation energies [51–55] suggest that this process would, at best, be slow, but it has been shown [56, 57] that significant quantities of β-Si_3N_4 can form on pure single crystal silicon when melting can be safely ruled out. Furthermore, the β-Si_3N_4 spikes are seen growing into "clean" pores where N_2 appears to be excluded. There is also no possibility that the structure grows by reaction with solid silicon. Other experiments show [58, 59] that a liquid does not necessarily enhance the rate of nitridation (eutectics of tin, zinc and copper).

Thus, there are conflicts between some of the proposed reaction mechanisms currently in the literature and inconsistencies between theory and observation. An attempt will be made to resolve some of these points.

3. Proposed theory of reaction mechanisms

Because data are being assembled from a large number of sources, the general theory will be presented first and then some consequences will be discussed. Insufficient data exists for the ideas presented here to be fully comprehensive, nor should it be concluded that the proposed mechanisms are the only ones that can possibly operate. Part II [60] will discuss some recent results and, in part, relate them to ideas discussed here.

Before the reaction starts gaseous nitrogen is in contact with the surface of solid silicon. As the temperature is raised, the reaction starts and either (a) nitrogen dissociates and then combines with silicon or (b) silicon moves to combine with a nitrogen molecule. The main idea behind the theory to be discussed here is the possibility that the former situation leads to β-Si_3N_4 and the latter to α-Si_3N_4. Since a solid-state reaction is not likely to occur, except possibly during early surface reaction, silicon is mobile when it enters into the reaction, it is either a liquid or a gas. If nitrogen is atomic (sometimes called active nitrogen, to be discussed later) and therefore also completely mobile, the more symmetrical and naturally bonded ($d\pi$–$p\pi$ [21]) β-Si_3N_4 structure may result. If molecular nitrogen enters into the original complexing process, steric hindrance may result in the more strained α-Si_3N_4 structure.

These two types of reaction will each have rate limiting processes. Either silicon or nitrogen or both must be transported to the reaction site and there must be sufficient space available for the product to form before the reaction can take place. Both the transport of reactants and/or creation of space can be rate determining and therefore must be considered part of the mechanism.

3.1. Product development

3.1.1. Initial surface reaction

In the absence of a substantial oxide layer on the silicon surface, the initial reaction is a nucleation and growth process [1, 60]. Small crystals form and as reaction proceeds they gradually cover the surface, eventually separating the reactants. The size and growth rate of the nuclei critically depends on reaction variables [8] such as temperature and pressure.

The formation of nuclei of Si_3N_4 is probably, at least in part, epitaxial. (i) There is X-ray evidence [60] that the (0 0 1) Si_3N_4 is almost parallel to the (1 0 0) silicon substrate, particularly in the initial stages of reaction. Other preferential orientations with respect to various silicon substrates have also been observed. Another observation [60] is that there is very often an unidentified

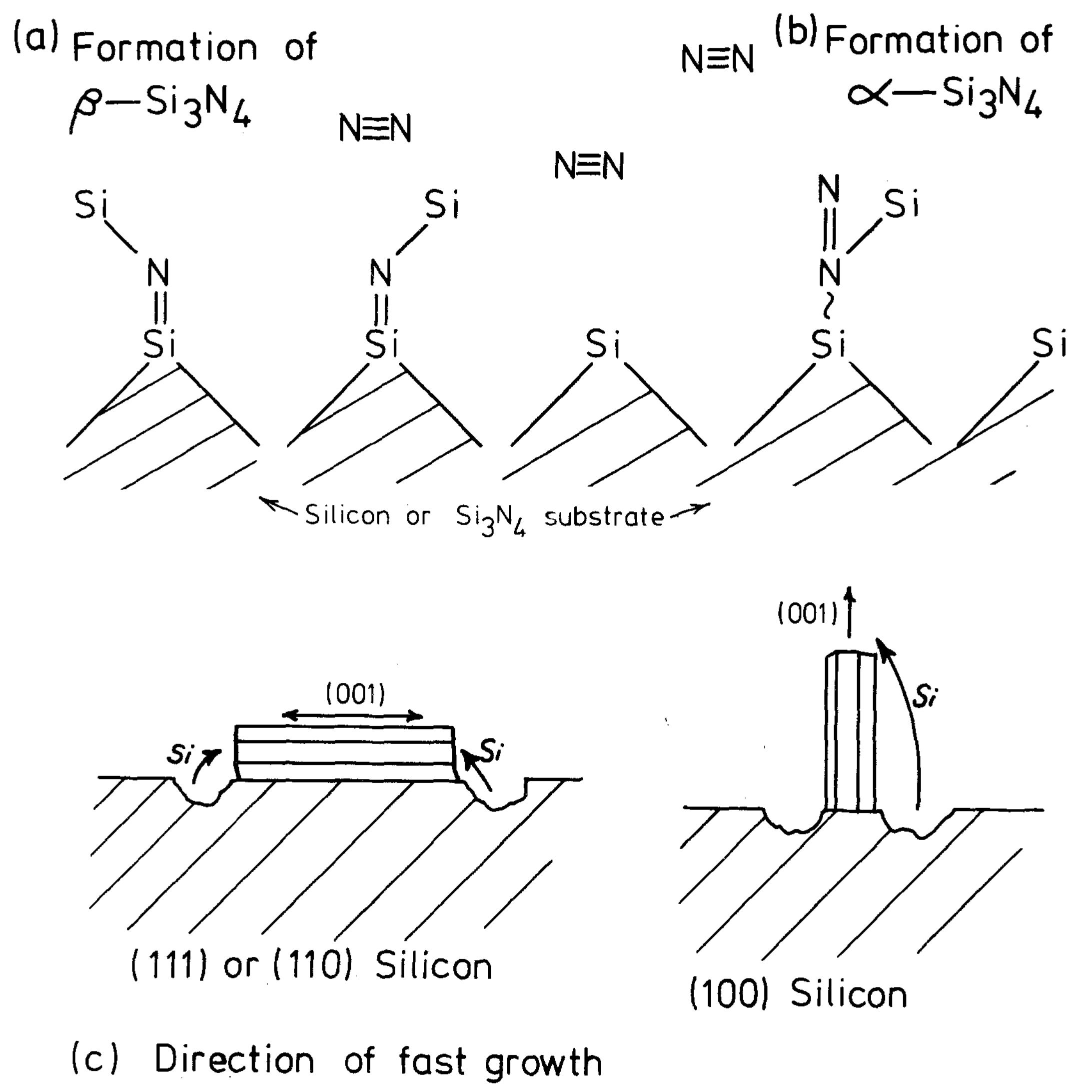

Figure 3 Formation of initial Si_3N_4 layer. (a) Formation of nuclei. Beta Si_3N_4 forms as dissociated nitrogen reacts and alpha Si_3N_4 forms as molecular nitrogen reacts. The orientation of the nuclei depends on substrate orientation. (b) The nuclei grow in the z-direction. Morphology and rate at which surface is covered depends on substrate orientation.

X-ray peak from a planar spacing of about 0.27 nm. This is almost exactly twice the spacing of the silicon (4 0 0) plane and it is possible that a reconstruction of the silicon surface, which allows the (2 0 0) plane to reflect, takes place during the early surface reaction. This reflection has been observed elsewhere [61] and never satisfactorily explained. (ii) Further support for epitaxial nucleation comes from the fact that liquid silicon and nitrogen do not react [48–50] until nuclei have somehow been introduced into the system (i.e. homogeneous nucleation appears difficult). This may be explained by noting that a liquid does not provide a crystalline substrate for initial reaction. (iii) The observation that either phase can be preferentially formed in the presence of "seeds" of that phase [36] is further evidence of the importance of the crystalline substrate. (iv) Finally, differences in product morphology with substrate orientation [56, 57, 60] may be linked to initial epitaxy.

Continued reaction takes place on available surfaces and unreactive nitrogen probably begins the process of dissociation only after it has adsorbed on a surface, Fig. 3. This is because atmospheric dissociation is usually observed only in the presence of a few types of other atoms such as helium [48, 62]. Furthermore, the obser-

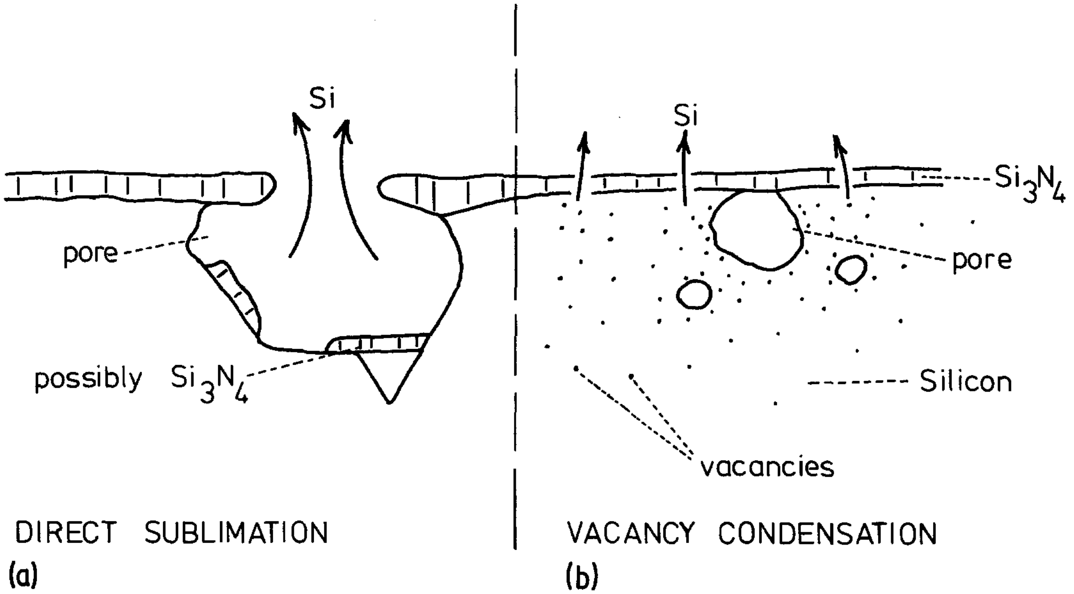

Figure 4 Two mechanisms for forming porosity, (a) direct volatization and (b) vacancy condensation. In the first case the pore may be open, nitrogen may enter and form Si_3N_4.

vation of "seeding" [36], where α- or β-Si_3N_4 encourage the continued formation of the same phase, also lends support to the idea that reactants adsorb on a surface before reacting. A surface reaction explains the fact that many substrates, such as alumina furniture, in the furnace never become coated with Si_3N_4 in spite of silicon and nitrogen in the atmosphere. The characteristics of the surface must be as important as the presence of silicon and nitrogen.

After nucleation, Si_3N_4 grows. It is probable [50, 56, 57, 60] that silicon nitride has a very strong tendency to grow in the z-direction. Thus, unless there are extenuating circumstances, crystals with high aspect ratios will form. Indeed poisoning of growth in other directions by impurities such as oxygen, may enhance this effect, a process which may be particularly important during the growth of long α-Si_3N_4 needles. On the other hand, rapid nucleation could result in small crystals. If the fast growing direction is parallel to the substrate, which appears to be the case on (1 1 1) and (1 1 0) silicon [60], then the nuclei will grow rapidly along the surface. This may encourage the sealing off of unreacted silicon. If not, i.e. (1 0 0), then the nuclei will attempt to grow perpendicular to the surface. Fig. 3 illustrates some of these possibilities.

It should be noted that in the presence of an oxide layer, reaction can only proceed after its removal. Thus the presence of oxides can cause an induction or dormant period before substantial reaction begins [9]. Impurities such as iron and hydrogen shorten the induction period.

3.1.2. Continued reaction: rate limiting step

If the reaction takes place outside the boundaries of silicon (forming "outer product") there is no problem with space. Silicon must simply be transported to the reaction site, and this is probably rate determining. It will be discussed later.

In the absence of melting, silicon will not flow from within the original boundaries; this means that space must be created before the "inner product" can form. Either silicon volatilizes and escapes through gaps in the nitride layer above a developing pore [8], or vacancies are created along the surface as silicon escapes and then they condense into pores [63], Fig. 4. Although the second option has been ruled out [8], it may be important in some cases [57, 64]. Both mechanisms require that silicon can escape from the surface and it is probable that the large silicon atom, much larger than nitrogen, does not diffuse through Si_3N_4. In the first case the rate that pores grow into silicon is limited by the rate that silicon escapes, while in the second the rate will depend on the self-diffusion coefficient of silicon.

The process of creating space requires that

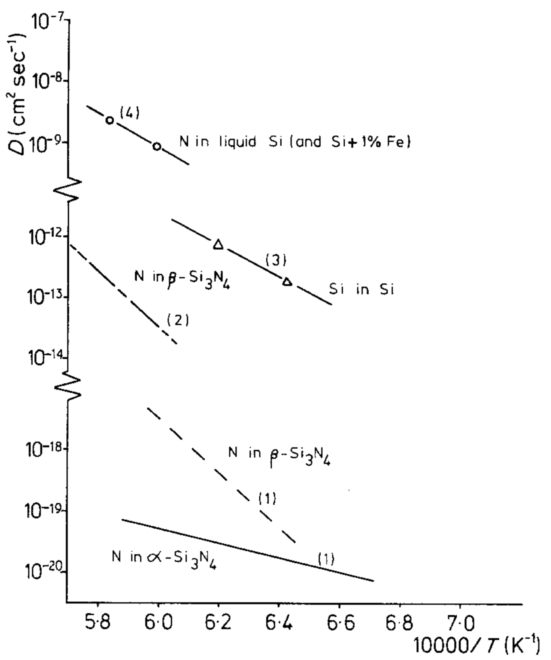

Figure 5 Diffusion coefficients relevant to the transport of silicon or nitrogen, curve (1) from [55], (2) from [51], (3) from [65] and (4) from [50].

silicon be moved to the outer area. It therefore passes nitrogen and the likelihood of it reacting on the way out or in the outer area may well depend on a number of reaction variables. If it adsorbs on a surface and nitrogen is reactive, then a product can easily form from the escaping silicon and this will tend to seal the porosity and thereby stop the reaction. On the other hand, if nitrogen is less reactive, or the surfaces are somehow poisoned or discourage adsorption of silicon, then this reaction may be retarded and therefore not seal off the underlying silicon. These ideas will be discussed further in Part II [60].

As the reaction front progresses into the silicon, nitrogen must be transported to the reaction site. If, without melting, silicon surface is directly exposed to nitrogen, i.e. if there is a large opening into a pore, then the rate that reaction front advances will be equal to the rate that porosity develops. This situation may occur when pores form faster than Si_3N_4 layer. If, however, nitrogen must be transported through the nitride layer (nitrogen has no solubility in solid silicon [48]) the rate will be limited by nitrogen diffusion, a process much slower than chemical reaction. Fig. 5 illustrates some diffusion data and it can be seen that diffusion of nitrogen in Si_3N_4 is, indeed, a slow step.

If silicon melts then both space for reaction product is easily created and an alternative diffusion path for nitrogen is provided, Fig. 2. The solubility of nitrogen in liquid silicon is fairly high [48] at 0.02%.

3.2. Formation of alpha and beta Si_3N_4

3.2.1. Comments on atomic nitrogen

There are several possibilities concerning how atomic (active) nitrogen might arrive at the reaction site. Firstly, although in gaseous atmospheres large quantities of nitrogen forms only under fairly specialized conditions, it is found in a wide variety of systems [62] even at one atmosphere pressure [66]. Environments which include high temperature, the presence of hot metallic surfaces [67–69], low pressure and the addition of helium [48, 70], krypton [71, 72] or argon [73] in N_2 gas contribute to the formation of atomic nitrogen. Other routes such as the decomposition of NH_3 [74], particularly in the presence of hot metals, can lead to atomic nitrogen.

$$N_2 + NH_3 \rightarrow NH + 2H + N_2 \qquad (5)$$

followed by

$$NH + H \rightarrow H_2 + N \qquad (6)$$

and

$$NH + N \rightarrow N_2 + H \qquad (7)$$

On the other hand, the presence of O_2, NO, NO_2, H_2 and H_2O [48, 75, 76] reduces the likelihood of atomic nitrogen. Oxygen impurities easily remove all active nitrogen. The recombination of nitrogen by reacting with NO appears to have almost no activation energy barrier [76], but like many of the nitrogen reactions it proceeds most easily on a surface. Most reaction conditions, therefore, discourage large quantities of atomic nitrogen in the atmosphere. The following reactions remove atomic nitrogen:

$$N + O_2 \rightarrow NO + O \qquad (8)$$

$$N + NO \rightarrow N_2 + O \quad \Delta H = -313\,\mathrm{kJ\,mol^{-1}} \qquad (9)$$

In the presence of H_2 and O.

$$O + H_2 \rightarrow OH + H \qquad (10)$$

followed by

$$N + OH \rightarrow NO + H \qquad (11)$$

Similarly NO_2 reacts with nitrogen in a number of ways [76].

Diffusion also demands the formation of atomic nitrogen. The large nitrogen molecule must dissoci-

TABLE I Thermodynamic data

Process	Pre-exponential cm^2 sec	Activation energy ($kJ\ mol^{-1}$) (per mole to form Si_3N_4)	Free energy change change of reaction ($kJ\ mol^{-1}$)	Reference
A Reaction with solid silicon (probably a mixture of diffusion of nitrogen in Si_3N_4 and surface reaction in pores)		652 661 418	-193 at 1683 K	52 53 54 (from Equation 1)
B Reaction with liquid silicon (diffusion of nitrogen in liquid)	$\sim 3.22 \times 10^{-8}$ (at 1683 K)	460	-192 at 1683 K	50 (from Equation 2)
C Reaction with gaseous silicon			-805 at 1683 K	(from Equation 3)
D Diffusion of nitrogen in β-Si_3N_4	1×10^{10} 6.8×10^{6}	777 776		51 55
E Diffusion of nitrogen in α-Si_3N_4	1.2×10^{-12}	233		55
F Diffusion of silicon in silicon	9×10^{3}	495		65
G Dissociation of Si–N bond		435		77
H Dissolve Si_3N_4 in silicon ($\alpha \rightarrow \beta$ Si_3N_4 transformation)		690 (1698–1823 K)		38
I Sublimation of Si_3N_4			740	25

ate before it will dissolve and diffuse through liquid silicon or solid Si_3N_4. In β-Si_3N_4 the channels in the z-direction are just able to transport a nitrogen atom [21]. It is interesting to note that diffusion in the β-Si_3N_4 structure has a high activation energy of about $750\,kJ\,mol^{-1}$ [51, 55]. This is approaching a value which is similar to dissociation energy of N_2, Equation 4. The high activation energy if off-set by a high frequency factor, Table I, resulting in a diffusion coefficient higher than that for α-Si_3N_4, Fig. 5, where the activation energy is lower. Similarly, nitrogen that diffuses to the reaction site through liquid silicon can also be considered atomic. The activation energy in this case is somewhat lower, $460\,kJ\,mol^{-1}$ [50] and the diffusion coefficient greater than in the case of Si_3N_4. If diffusion is the rate controlling step, the presence of liquid silicon between N_2 atmosphere and reaction site (assuming the path lengths are equal) would result in a much faster growth rate than would the process of supplying nitrogen to the reaction site by diffusion down β-Si_3N_4. In either case diffusion does not lead to α-Si_3N_4.

3.2.2. Formation of β-Si_3N_4

The thermodynamics of three possibilities concerning reaction paths which lead to β-Si_3N_4 are illustrated in Fig. 6. The reaction progresses from left to right along one of the paths indicated. Energy changes, relative to the starting material, are represented by the height of the curve. The dotted lines indicate that the activation energies are not known. The energies associated with chemical changes and intermediates, labelled A to I, are taken from Table I. The reaction will proceed most rapidly, of course, along the available path with lowest energy. The rate will depend on the highest energy or "activation" energy and the pre-exponential frequency factor. The available path may change with reaction conditions and with time.

Initial formation of β-Si_3N_4 is represented by curve 2, where nitrogen dissociates and then reacts on the silicon surface. For continued reaction, β-Si_3N_4 may grow into a pore which will contain only silicon vapour. Diffusion through the β-Si_3N_4, path 1, Fig. 6, requires a large amount of energy and, if operating, growth will be slow. Reaction takes place on the β-Si_3N_4 surface. In the absence of other routes, particularly nitrogen through a liquid, it may be the only way for continued β-Si_3N_4 growth has been observed [56, 60]. If pores are open, nitrogen which enters the porosity, enters a clean environment, i.e. no O_2 and, if N_2 is pure and can dissociate, nucleation of β-Si_3N_4 may be favoured thus filling pores. As the reaction proceeds adsorbed silicon vapour may react, sealing the pores and slowing the reaction and/or forming "outer" product. These reactions follow path 2, Fig. 6.

If silicon melts nitrogen can diffuse through the liquid and the reaction follows path 3, Fig. 6. This has the lowest activation energy and there-

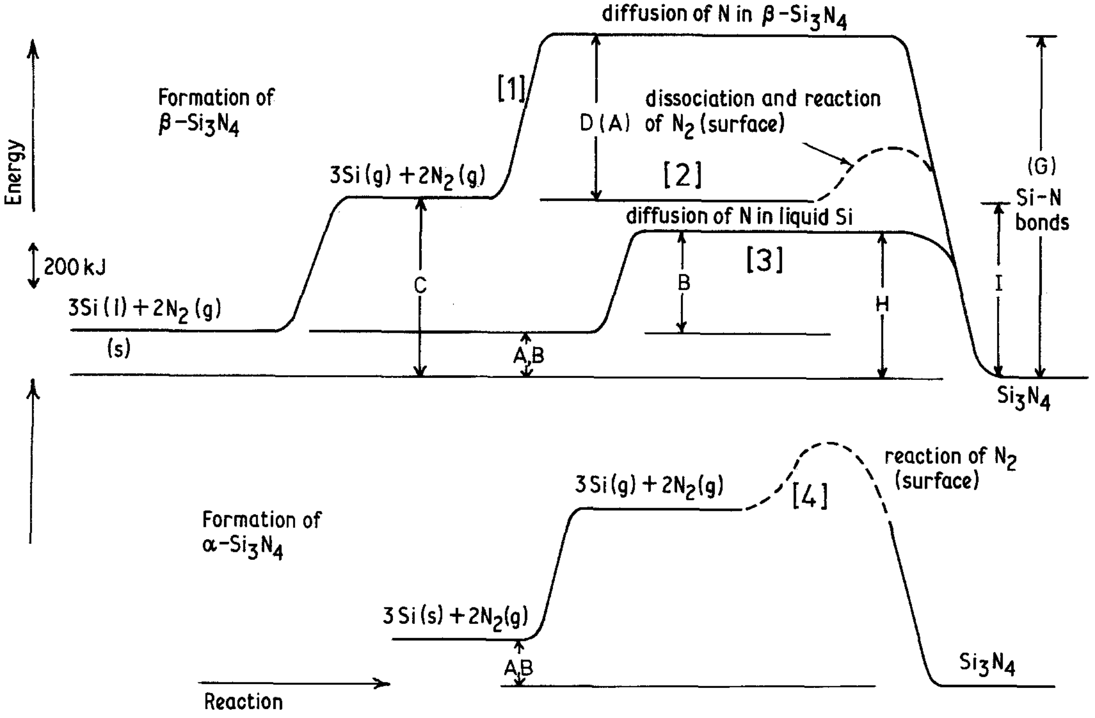

Figure 6 Thermodynamic reaction paths leading to α- and β-Si_3N_4. Data is taken from Table I. Note: (i) the activation energy for Si_3N_4 growing into a solid (Table I) is less than diffusion of nitrogen in β-Si_3N_4 (as above). This is assumed to be because the experimental rate of Si_3N_4 growing into solid (probably producing both α- and β-Si_3N_4) also includes surface reactions which have a lower activation energy. (ii) The data for dissolution is obtained from experiments on $\alpha \rightarrow \beta$-Si_3N_4 transformation through a liquid. Because the free energies of α- and β-Si_3N_4 are roughly the same, the activation energy of dissolution for both phases are roughly the same. (iii) Dotted line indicates activation energy is not known.

fore the fastest kinetics. Large β-Si_3N_4 crystals dominate when a liquid is present [1, 12, 50]. Further evidence for diffusion through liquid silicon is supplied from the observation [50] that it must be saturated with nitrogen in order to prevent Si_3N_4 dissolution. As noted by Mukerji and Biswas [50], when the reaction has progressed to a point where the surface of the molten silicon is completely covered with Si_3N_4, nitrogen diffusion through Si_3N_4 may again become important. For paths 1 and 3 the rate controlling step is diffusion and the pre-exponential terms are known. Thus the rates can be determined from Fig. 5.

In constructing the argument outlined above, support has been gained from the fact that decomposition of β-Si_3N_4 can be interpreted as reactions going from right to left in Fig. 6. Thus, sublimation energy is that required to form elemental gases while the energy required to break $3\frac{1}{2}$ Si–N [77] bonds produces gaseous silicon and atomic nitrogen. The volatization of Si_3N_4 may involve the formation of SiN_2 structures [67]. In a sense the β-Si_3N_4 reaction is reversible.

3.2.3. Formation of α-Si_3N_4

Somewhat less detailed data exists for the α-Si_3N_4 phase. It is, however, generally thought that it forms from a gas phase reaction. Indeed, after an initial reaction layer is formed the only way that silicon can react with molecular nitrogen is for silicon to first vaporize. Fig. 6 illustrates a possible route for α-phase formation.

In the initial stages silicon may react with molecular nitrogen during the dissociation process to form α-Si_3N_4 nuclei, Fig. 3. As reaction proceeds silicon will volatize and combine with molecular nitrogen, probably on a convenient surface. Thus, reactions which form α-Si_3N_4 always take place in a predominantly nitrogen environment, and very often this will be outside the boundaries of the original particles ("outer" product).

It was not possible to deduce the activation energy associated with this reaction. Volatization of silicon and some activation energy associated with the break up and reaction of molecular nitrogen are both contributing. Like most of these reactions the presence of the silicon nitride substrate is probably very important.

No sensible reverse reaction could be deduced. The decomposition of α-Si_3N_4 may not occur by a reaction path which is simply the reverse of the forward reaction path.

4. Discussion of theory

A strong test of a theory is its ability to explain various observables including the influence of reaction variables on kinetics and type of product. This section will discuss some of these observables with reference to the proposed theory.

4.1. $\alpha \rightarrow \beta$ Si_3N_4 conversion

The reaction mechanisms outlined here can easily explain $\alpha \rightarrow \beta$ Si_3N_4 transformation, the fact that it is almost always observed in the presence of a liquid and the fact that $\beta \rightarrow \alpha$ Si_3N_4 is never observed. Either phase decomposes either by dissociation or by dissolution, the latter is energetically by far the easier, path 2, Fig. 6. In the presence of a liquid, Si_3N_4 will dissolve and nitrogen, as already discussed, will be atomic. The only subsequent product possible, in this scheme, is β-Si_3N_4. Thus, liquid [35, 38–40] facilitates transformation. Since β-Si_3N_4 may be slightly more stable than α-Si_3N_4 the driving force will also favour the transformation.

4.2. Influence of reaction variables

Table II outlines the influence of a number of reaction conditions on the α/β ratio of product, the texture of product, the character of porosity, the reaction kinetics and the percentage reacted before the reaction comes to a stop.

4.2.1. Kinetics

Under various reaction conditions certain reaction routes may be forbidden or encouraged. From the preceding discussion it can be seen that the energetics leading to α- and β-Si_3N_4 may be similar, and the amount of either product formed depends on the availability of a reaction route and the relative kinetics.

Thus the overall kinetics of formation of Si_3N_4 is the sum of separate kinetics for α- and β-Si_3N_4 formation and further, the reaction route and associated kinetics forming either phase can change with changing conditions, such as temperature, and the passage of time. The kinetics of a particular reaction path depend on the activation energy. For present purposes this can be divided broadly into two types: (a) diffusion of a reactant to the reaction site or the creation of space by transport of silicon, or (b) the chemical reaction of gaseous reactants, probably on a convenient surface. The composition of the gas influences the second type but not the first. Impurities in liquid silicon can influence the first but diffusion in Si_3N_4 depends only on temperature. No pre-exponential frequency term is available for gas phase reactions so that Fig. 6 can only serve as a rough guide to these kinetics. Diffusion coefficients, rate controlling for the second type of reaction, contain this term and are a much more accurate guide to those reaction rates.

When considering overall kinetics attention must also be paid to the fraction of material that is involved in a particular reaction. For example, as the reaction continues the amount of silicon surface will be reduced and this reduces silicon vaporization which will reduce vapour phase reactions. This paper, therefore, will only establish some trends and not the details of reaction kinetics.

The final percentage reacted depends on how soon silicon is sealed away from the nitrogen. At temperatures below melting this will depend on how quickly silicon is prevented from leaving the surface and creating pores for nitride to grow. (It is assumed that nitrogen can slowly diffuse inwards but the large silicon atoms probably will not diffuse through a nitride layer.) Without space the reaction will stop. Furthermore, obviously, if silicon does not diffuse outwards there is no "outer" reaction. The rate at which the product seals the surface will depend on the relative kinetics of silicon volatization (pore formation) and product formation. A tight fitting, fine grained product will be most effective at stopping the reaction.

4.2.2. Examples of the influence of reaction variables

Reaction variables can only encourage certain products as outlined in Table II. Volatization of silicon, or the formation of a fine, closely packed product which might seal under-lying silicon, or the formation of active nitrogen might all be encouraged but, because there is almost always more than one reaction route available, the influence of reaction variables will only encourage the formation of a given product while other products form at a slower rate. For example, even when active nitrogen is encouraged in the gas it

TABLE II Influence of reaction variables on product

Reaction variable		Influence on product	Influence on kinetics and final % reacted	Outline of an explanation
Time		Early reaction produces high α/β-Si_3N_4	Reaction rate decreases with time	Oxygen associated with surface encourages α-Si_3N_4 As reaction proceeds silicon is sealed
Low temperature (< 1350° C)		High α/β-Si_3N_4 Fine structure [8]	Slow reaction rate [8] Small % reacted	Thin nitride layers covers surface
		(Comparing with above)	(Comparing with above)	
Medium temperature (1350–1410° C)		Texture becomes coarser with increasing temperature [8] Pore size increases [56,57]	Extends linear kinetics [8] Increases rate [8] Increases % reacted [8]	Encourages diffusion and volatization of silicon and formation of porosity
High temperature (> 1410° C, Si melting)		Strongly encourages β-Si_3N_4 formation Coarsens structure	Increases % reacted	Presence of liquid encourages fast diffusion of nitrogen and allows silicon to flow to and from reaction site
Surface area		α/β-Si_3N_4 increases with increasing surface [12]	Reaction rate increases with increasing surface Increases % reacted	Oxygen associated with surface encourages α-Si_3N_4 Surface reaction may involve molecular nitrogen Reaction proceeds further before underlying silicon is sealed
Pressure (medium temperature)		Texture becomes finer with increasing pressure [8]	Early linear rate increases with increasing pressure [8] High pressure reduces % reacted, i.e. linear rate terminates sooner [8]	High pressure increases nucleation rate High pressure encourages product to form rapidly over entire surface
Flowing gas may influence concentration of impurities, i.e. oxygen may be removed	Oxygen	Increases α/β-Si_3N_4 [26, 27, 43, 45, 46]	Little change in kinetics [26, 27, 43, 45, 46] Initial dormant period is lengthened [9]	Discourages reduction of initial silica layer Increases SiO but this may not react Discourages the formation of atomic nitrogen
	Hydrogen	Increases α/β-Si_3N_4 [5] Texture becomes finer [5]	Increases kinetics [1, 5] Shortens initial dormant period [9] Increases % reacted [1, 5, 9]	Encourages reduction of silica layer Encourages reaction of SiO Discourages atomic nitrogen
Iron		Increases β-Si_3N_4 at high temperature	Increases % reacted Shortens dormant period [10]	Encourages reduction of silica layer Encourages melting and fast diffusion of nitrogen Encourages atomic nitrogen
Flowing nitrogen atmosphere		Encourages clean porosity [56, 57]	Not clear	Removes silicon. Encourages porosity Removes or introduces impurities
Heating rate		Various heating rates appear to alter α/β-Si_3N_4 [12]	Not clear	Early reaction influences later reaction

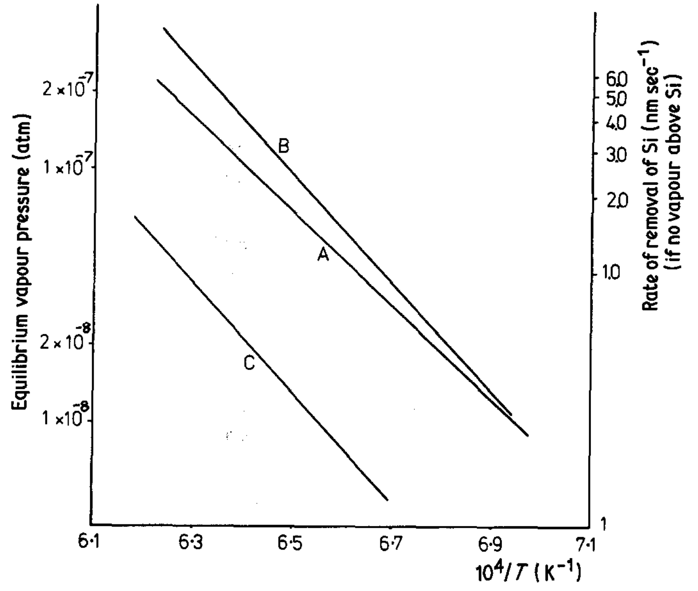

Figure 7 Evaporation and equilibrium partial pressure over silicon substrate against temperature.

will almost always co-exist with molecular nitrogen and therefore both α- and β-Si_3N_4 will form simultaneously. In addition some reaction variables may encourage atomic nitrogen but others, for example the presence of even small amounts of oxygen, will override the first effect.

The influence of reaction variables will be considered in two parts, (a) influence on silicon, i.e. melting temperatures, diffusivity etc., and (b) influence on nitrogen, i.e. reactivity. The former has been considered in the literature but the latter has not. Part II [60] will discuss the influence of some new variables.

4.2.2.1. Surface area. Like many variables, the role of particle size or surface area is interlinked with other reaction variables. Because even small amounts of oxygen can remove active nitrogen, most surface reactions will produce α-Si_3N_4 (surfaces will generally be coated with oxides). The initial product will influence later product and therefore high surface area will generally imply high α/β Si_3N_4 ratio [12]. The contrary may be true for very pure systems [5]. Also, high surface area will mean that a high percentage of product will be formed before unreacted silicon is sealed from the nitrogen.

4.2.2.2. Temperature. The viability of a given reaction path is influenced by temperature as already discussed. Diffusion, which is the rate controlling step for some of the paths, is very sensitive to temperature (high activation energy). Hot surfaces, in the absence of oxygen, are a potential source of atomic nitrogen and since dissociation requires a lot of energy this process is also strongly temperature dependent. In addition, there are other effects of temperature.

The equilibrium vapour pressure over condensed material can be written as

$$p = A \exp\left(-\frac{L}{RT}\right) \qquad (12)$$

where p is the vapour pressure, L is the heat of sublimation (for Si = 442 kJ mol^{-1} at 1410° C), R is the gas constant, T is the absolute temperature, and A is an "integration" constant. p is strongly temperature dependent, but does not depend on the pressure of other gases. Moulson [1] has pointed out that at 1350° C, $p = 10^{-7}$ atm and this implies an evaporation rate of 10^{-6} kg m^{-2} sec^{-1} [78]. This rate can supply more than enough vapour to explain observed vapour phase reactions – 10^{-7} kg m^{-2} sec^{-1} silicon consumed. Fig. 7 illustrates more recent data [79–81] on rate evaporation of silicon from pure substrates. (This rate may be significantly altered from impure substrates.) Included is the calculated equilibrium partial pressure of silicon [82], using the Dushman formula. As can be seen there is a strong temperature dependence with more rapid vaporization at higher temperature. Since the overall loss of material is equal to the difference between rates of evaporation and condensation, and since the rate of condensation will be equal to the rate that atoms strike the surface [79], the overall rate of

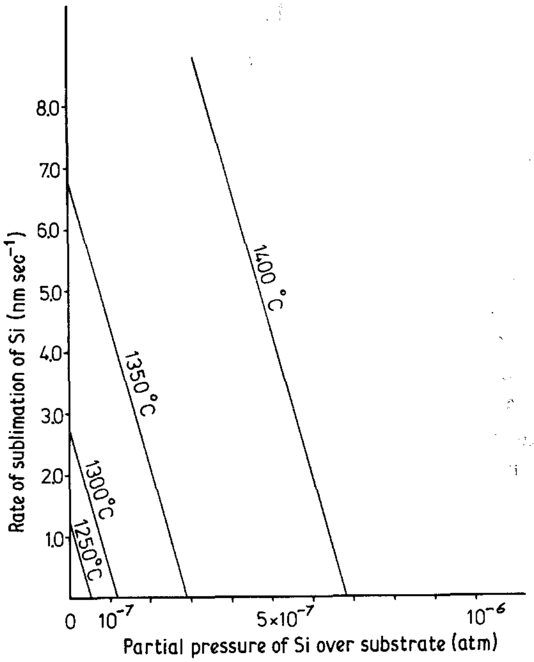

Figure 8 Partial pressure of silicon over substrate against rate of removal of silicon (using curve A from Fig. 7). Curve A from [80], curve B from [81], curve C from [82].

removal of silicon will depend on the partial pressure of silicon above the substrate. Thus a family of curves, Fig. 8, for the rate of removal of silicon can be drawn. Formation of porosity, both by direct evaporation and by creation of vacancies, and therefore the ability to create space within silicon without melting, depends strongly on silicon partial pressure. Because of the rate of self-diffusion of vacancies into silicon and the rate of evaporation of silicon are comparable with the rate of nitrogen diffusion into Si_3N_4, the creation of space could become rate limiting under conditions of high partial pressure, which is influenced by temperature, vapour phase reaction and gas flow rate (which could remove silicon).

During early stages of reaction and at low partial pressures of silicon and at high temperature and/or with flowing nitrogen, silicon will be rapidly removed from surface, Fig. 8, which may discourage nitrogen adsorption and nucleation of Si_3N_4. High temperature implies fewer particles nucleating and this will imply a coarse structure and extended linear kinetics as has been observed [8]. High temperature also implies a greater possibility of losing silicon [60].

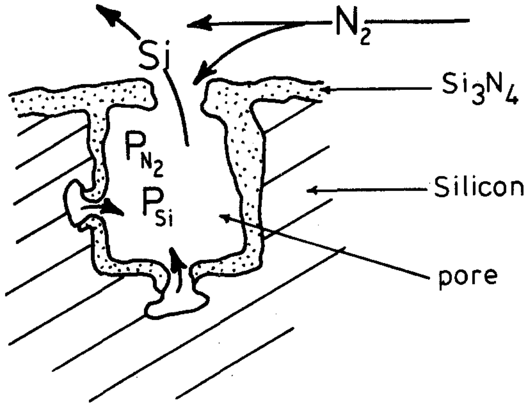

Figure 9 Schematic representation of silicon escaping from small pores through a narrow opening into a larger pore area where it can react with nitrogen. The large pore might be the original void space in a powder compact and this might be open to the nitrogen atmosphere.

Temperature will effect the rate of the heterogeneous surface reaction in the normal way. A rate constant can be written as:

$$K = A p_{Si} p_N \, e^{-\Delta E^+/RT} \qquad (13)$$

The pre-exponential "frequency" factor is a function of activation entropy, and p_{Si} and p_N are partial pressures of gaseous reactants above the surface where the reaction takes place. Thus, if the reaction takes place on Si_3N_4 (i.e. not on silicon) the pressure of silicon vapour, as well as energy to overcome activation barrier, ΔE^+, are important, and they both depend on temperature. Unfortunately, it has not been possible to evaluate activation entropies or energies for any gas phase reaction and therefore only trends can be discussed.

It is interesting to note that the partial pressure of silicon must be maintained at some finite value for a reaction involving the transport of silicon as a vapour to proceed at a non-trivial rate. This is important when forming "outer" product. Maintenance of p_{Si} in a pore between nitriding grains, Fig. 9, which is open to the nitrogen atmosphere, requires that silicon evaporates from available surfaces at a rate equal to the reaction rate (or slightly greater as some silicon escapes into the atmosphere). Reduction of silicon surface as product forms and small passages connecting clean pores with "outer" interparticle pores, Fig. 9, could significantly reduce p_{Si} in the interparticle pores and this, in turn, could slow the formation of "outer" product.

4.2.2.3. Pressure. The density of Si_3N_4 nuclei depends on the amount of adsorbed nitrogen (and silicon) and this, in turn, depends on pressure. Reaction rate also depends on pressure as already discussed, Equation 13. High pressure will form many nuclei and will increase initial kinetics and thus a fine structure which seals the surface and quickly stops reaction will result, as has been observed [8].

Concerning the overall per cent reaction the partial pressure of silicon is important, particularly at high temperature, Fig. 8, both for the creation of porosity and the rate of gas phase reactions. High partial pressure of silicon will encourage rapid gas phase reaction to produce a finely textured product which could seal surface, and also it discourages the formation of porosity, both of which stop the reaction as has been observed [8].

4.2.2.4. O_2, H_2 and H_2O. The effects of these gases on the vaporization and subsequent reaction of silicon have been considered by Moulson [1]. The following reactions were used.

$$2\mathrm{Si} + \mathrm{O}_2 = 2\mathrm{SiO}$$

$$\Delta G = -477\,\mathrm{kJ\,mol^{-1}}$$

$$= -RT\ln\left(\frac{p^2_{\mathrm{SiO}}}{p_{\mathrm{O}_2}p^2_{\mathrm{Si}}}\right) \qquad (14)$$

$$K = \frac{p^2_{\mathrm{SiO}}}{p_{\mathrm{O}_2}p^2_{\mathrm{Si}}} = 5\times10^{14}\,\mathrm{atm}$$

and at the reaction temperature

$$3\mathrm{SiO} + 2\mathrm{N}_2 = \mathrm{Si}_3\mathrm{N}_4 + \tfrac{3}{2}\mathrm{O}_2$$

$$\Delta G = 502\,\mathrm{kJ\,mol^{-1}}$$

$$\ln\left(\frac{p^{3/2}_{\mathrm{O}_2}}{p^2_{\mathrm{SiO}}p^2_{\mathrm{N}_2}}\right) = -\frac{\Delta G}{RT} \qquad (15)$$

$$K = 7\times10^{-17}$$

Analysis indicates that for SiO to contribute to nitridation, when it has formed at typical oxygen partial pressures, i.e., $p_{\mathrm{O}_2} \simeq 10^{-5}$ atm and $p_{\mathrm{Si}} \simeq 10^{-8}$ atm, it must find a reaction zone with extremely low oxygen partial pressures, i.e. $p_{\mathrm{O}_2} \simeq 10^{-19}$ atm. The process is unlikely. Possibly, if SiO_2 rapidly decomposes and the vapour spreads in such a way that it remains stable, subsequent nitridation will occur in an area of low p_{O_2}. The removal of surface silica could produce this situation. Oxygen, however, can remove silicon which creates space and therefore encourages reaction.

Water will react with silicon

$$\mathrm{Si} + \mathrm{H_2O} = \mathrm{SiO} + \mathrm{H}_2 \qquad \Delta G = -84\,\mathrm{kJ\,mol^{-1}} \qquad (16)$$

also

$$\mathrm{H_2O} = 2\mathrm{H}_2 + \mathrm{O}_2 \qquad \Delta G = 314\,\mathrm{kJ\,mol^{-1}}$$

$$K \simeq 10^{-10} \qquad (17)$$

Similar arguments can be used to show that water makes no contribution to nitridation. Water and/or oxygen could, however, help create vital porosity.

A very important consideration is that all of this analysis assumes equilibrium which, because of high activation energies and slow kinetics, may not apply. For example, the relative kinetics of Equations 14 to 17 will determine the partial pressures. If Equation 17 is a slow reaction compared to Equation 16 the influence of H_2O may be important. H_2O has been observed to increase the reaction rate [1].

As pointed out by Moulson [1] hydrogen can strongly reduce the p_{O_2}. In the presence of excess H_2 Equation 17 goes to the left and consumes oxygen. $p_{\mathrm{O}_2} < 10^{-19}$ to 10^{-21} atm can be achieved if $p_{\mathrm{H_2O}}$ is between 10^{-8} to 10^{-6} atm which is possible when 0.1 to 10% H_2 is added to nitrogen. Nitridation may be encouraged by hydrogen.

At temperatures above melting the energetics of β-Si_3N_4 forming as nitrogen diffuses through a liquid and α-Si_3N_4 forming from gaseous reactants are similar, Fig. 6. However, even if volatilization of silicon is encouraged by the presence of oxygen, increased reaction rate leading to α-Si_3N_4 is not expected. Rapid formation of β-Si_3N_4 is the major reaction route.

Impurities can influence the reactivity of nitrogen. As already discussed environments containing oxygen and hydrogen strongly discourage atomic nitrogen. Thus, H_2 has the two roles of discouraging active nitrogen and encouraging reduction of SiO. H_2, therefore, will not only increase the rate of formation of α-Si_3N_4 but decrease the rate of formation of β-Si_3N_4 (on clean open pores etc.) as has been observed [5]. It should be noted that hydrogen may be generated in a number of ways, i.e. Equations 5 to 7, 10, 11, 16, 17, and thus the role of impurities may be multiple. The absence of active nitrogen will slow vapour phase reactions (on surfaces) which will help prevent pores from being sealed and thus a greater per cent reaction will be observed [1, 5, 9]. These gases could also help slow the process of diffusion by slowing the formation of atomic nitrogen.

Finally, oxygen could poison the growth of Si_3N_4 in some directions. Indeed, α-Si_3N_4 needles with a sheath of oxide have been observed [83].

4.2.2.5. Iron. Many metals can catalyse the removal of a protective oxide layer, and iron has been shown to promote this effect in nitridation of silicon [10]. Furthermore, it is well-established that metals reduce the melting temperature of silicon and this, in turn, promotes the formation of β-Si_3N_4. The diffusion constant of nitrogen in liquid silicon is the same with or without iron, iron simply enhances melting [50]. Other metals alter the diffusion constant, i.e. titanium and hafnium increase the diffusion rate [50].

In the light of arguments presented in this paper iron could also influence the nitrogen atmosphere. For example, it is a known catalyst in the formation of NH_3 which is a potential source of atomic nitrogen, i.e. Equations 5 to 7. In the presence of H_2 or H_2O this could become significant, which means that, as discussed in Part II [60], iron may influence the reaction without being in physical contact with silicon.

4.2.2.6. Static or flowing nitrogen over silicon. The influence of flow rate on the reaction has not yet been fully explained. Impurities are either brought into or swept away from the reaction site. Most impurities discussed here discourage active nitrogen and therefore slow the formation of β-Si_3N_4 in the early stages where surface reaction predominates.

At high temperature a small drop in silicon vapour pressure will greatly increase the rate of evaporation, Fig. 8. Thus, another possible role of flowing N_2 is to remove silicon vapour and lower its partial pressure, this will encourage pores and coarse product (and reduce mechanical strength) as has been observed [4, 5]. Also turbulence may help nitrogen enter porosity.

4.2.2.7. Heating rate. Many reaction variables including temperature, influence the type of product formed during the early stages. Lower temperature generally encourages α-Si_3N_4 but because it forms as a fine grained matt the reaction may quickly stop. Also the formation of α- or β-Si_3N_4 can depend on the presence of either of the two phases [36]. Thus product formed during the early stages of reaction can influence the final α/β Si_3N_4 ratio. This implies that heating rate or time spent at a given temperature could influence the final α/β Si_3N_4 ratio as has been observed [12].

5. Intention of theory

This paper does not answer all questions. For example, the early observation that α-Si_3N_4 can form from a liquid [84] is contrary to the ideas discussed here. Other mechanisms may, therefore, operate and further research on many ideas proposed here, such as detailed kinetics, is necessary. The intention of this paper is to suggest possible mechanisms (admittedly partly speculative) which can serve as a basis for further discussion and research. It is hoped that experiments will help confirm or deny these ideas and in the process a deeper understanding will be achieved.

6. Conclusions

1. There are probably several reaction mechanisms leading to both α- and β-Si_3N_4. Each mechanism has separate energetics and rate controlling step. A generalization, however, can be made: α-Si_3N_4 involves the reaction of molecular nitrogen while β-Si_3N_4 involves atomic nitrogen. This provides a framework for examining detailed reaction mechanisms. They can be made compatible with a wide body of observations. Many of the existing theories are correct for specific reaction conditions.

2. The overall kinetics can be considered the sum of separate kinetic laws.

3. Controversy in the literature concerning the necessity of a liquid for β-Si_3N_4 formation is resolved by noting that the presence of liquid silicon, although not necessary, provides an easy diffusion path for nitrogen, which will be atomic, and result in β-Si_3N_4 growth. If a liquid is not present, however, β-Si_3N_4 slowly forms from nitrogen which diffuses through the crystal.

4. Both α- and β-Si_3N_4 can form from gas phase reactions but the reactions probably take place on a solid surface, either silicon or Si_3N_4, and they are probably epitaxial.

5. Under specific conditions only some reaction paths may be available. The α/β Si_3N_4 ratio will result from a kinetic competition between the available paths.

6. An energetic difference between α- and β-Si_3N_4 which would imply a high and low temperature phase is small and the transformation

difficult. The more strained and less symmetrically bonded α-Si_3N_4 may form because of steric hindrance when silicon is complexing with nitrogen molecule.

7. Many impurities are known to effect the reaction through their effect on silicon, i.e. encourage volatization or melting. Impurities may also effect the reactivity of nitrogen and this is an area that has not received the attention it deserves in the literature. Reaction paths can be encouraged or discouraged by changing conditions; this may change α/β Si_3N_4 ratio.

8. The decomposition of Si_3N_4 is most easily achieved by dissolution. This produces atomic nitrogen (dissolved). Reprecipitation of product, therefore, must produce β-Si_3N_4. Thus $\alpha \rightarrow \beta$-Si_3N_4 transition is possible and $\beta \rightarrow \alpha$-Si_3N_4 is not.

9. In the absence of melting the creation of space by vaporization of silicon is necessary for reaction to continue. The rate of volatization is sensitive to vapour pressure, particularly at high temperature, and this in turn is effected by variables such as gas flow rate. The details of silicon vapour pressure are important to the reaction.

10. There may be a phase and structure difference between "inner" and "outer" product.

Acknowledgements

I wish to thank Professor P. L. Pratt for detailed reading of the manuscript and stimulating comments, L. Dutton and Catherine Young for help in preparation of the manuscript.

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Received 7 April
accepted 7 September 1982