Fluoride accelerated nitridation of silicon

D. CAMPOS-LORIZ, S. P. HOWLETT, F. L. RILEY, F. YUSAF
Department of Ceramics, University of Leeds, Houldsworth School of Applied Science, Leeds, UK

Fully characterized silicon powder has been nitrided alone, and in the presence of small amounts of aluminium, calcium and sodium fluorides. Comparisons of the overall extents of reaction, and individual α- and β-silicon nitride phase yields, have been made. It is concluded that the principal action of these fluorides is the disruption of the native silica film on the silicon surfaces, thereby increasing the active site density at which nitridation can occur. The nitridation kinetics are shown to be consistent with a "mutually blocking pore" model.

1. Introduction

From time to time reports have appeared in the literature concerning the use of metal fluorides as catalysts in the silicon nitridation reaction. In some cases reference is made only to the overall reaction rate [1–3]. Other authors report that certain fluorides (CaF_2, MnF_2, PbF_2) preferentially accelerate formation of the α-phase, whereas AlF_3 accelerates formation of the α-phase [4]. Some fluorides, LiF and NaF for example, have been claimed to be without effect [4], and there is disagreement over the action of CaF_2 and BaF_2 [1, 4]. In the cases where CaF_2 and BaF_2 are reported to have an effect, it appears to be relatively short-lived, and over longer periods of time the extent of the uncatalysed reaction of the same silicon powder may reach that of the catalysed process.

Although the general accelerating action of members of the metal fluoride group is undoubtedly a real one, no convincing explanation has ever been advanced for it. Recently, however, detailed studies have been made of the action of iron and hydrogen in the silicon nitridation reaction, both of which also have a considerable influence on the initial reaction rate [5–10]. These studies have contributed towards an improved understanding of the nitridation process, and point in particular to the importance of the native silica film [5] on the silicon surface. As a result it is now possible to provide an interpretation of the action of these metal fluorides. The work reported here concerning fluoride additions has formed part of a broad investigation into the effects of a range of additives on the separate rates of formation of the α- and β-phases of silicon nitride from a series of commercial silicon powders.

Fluorides in general present difficulties in the context of a reaction normally carried out in the temperature region of 1300 to 1400° C partly because of their relatively low melting points, but more importantly because of their volatility and the likelihood of consequent loss of material during the nitridation process. Calcium fluoride was therefore chosen as the principal additive for this study because of its high melting point (1418° C) and its low vapour pressure at the temperature of interest (approximately 10^{-5} atm. at 1365° C). Other materials examined in lesser detail were aluminium fluoride and sodium fluoride, both suffering from the disadvantage of volatility, aluminium fluoride extremely so.

2. Experimental

The characteristics of the silicon powder used for this study are shown in Table I. This powder had been used in earlier studies [11], and a new complete spectographic analysis revealed the presence of small amounts of copper and antimony not previously analysed for. Aluminium, sodium and calcium fluorides were of AnalaR or high purity grade and were mixed with silicon powder by high frequency shaking in a polyethylene bottle for

TABLE I Characteristics of the silicon powder

Median particle size (μm)	BET surface area ($m^2 kg^{-1}$)	Major impurity levels (at. %)						
		O	Al	Fe	Cu	Sb	Ca	Na
20	450	0.53	0.47	0.21	0.20	0.05	0.02	0.01

4 h. The silicon powder was compacted iso-statically without binder at 120 $MN m^{-2}$, small compacts of the order of 700 mg in weight being used for each experiment. The compacts were located inside small alumina tubes, approximately 50 mm in length and 25 mm diameter, the ends of which were then packed with zirconium foil as an oxygen getter. Isothermal nitridations were carried out at 1365° C in a resistance heated alumina tube furnace, using "white-spot" nitrogen with a flow rate of 50 ml min^{-1}. Measurements of oxygen and water partial pressures were not made, because it was assumed that these would be controlled at a low level in the reaction zone by the presence of the zirconium. The silicon compacts were weighed before and after reaction, and X-ray analyses for α- and β-silicon nitrides were made using CuKα radiation in conjunction with a Philips diffractometer. The α/β phase ratio in the powdered product was obtained from the use of a standard calibration chart, using measurements of the peak heights of the α_{102} and the β_{210} reflections. The analytical data were normally expressed in terms of the "phase yield", that is, the weight of α- or β-phase formed from 100 units of weight of silicon powder.

In most experiments a reference silicon powder compact was included in the reaction system. This was located close to, but not in contact with, the compact containing the fluoride. Its function was to detect possible interactions of silicon with

vapour phase species resulting from the presence of the additive.

3. Results

The results of preliminary experiments into the action of sodium, calcium and aluminium fluorides are shown in Table II. The reference compacts showed similar, but much less striking trends in behaviour, compared with the doped compacts. These data were obtained at a constant reaction time of 8 h. More detailed experiments were made with a range of nitriding times using 2 wt % calcium fluoride. The overall fraction of reaction as a function of time for compacts containing calcium fluoride, and for the reference compacts nitrided simultaneously, is shown in Fig. 1. Also shown in this figure is the reaction curve for the same powder nitrided alone. The separate yields of the α- and β-phases of silicon nitride formed from the calcium fluoride doped compacts, and the refer-

TABLE II Effects of fluoride additions: nitridations in nitrogen for 8 h

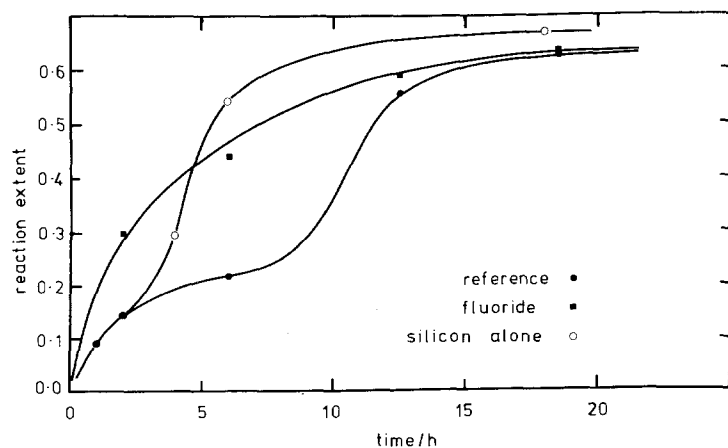| Additive	Quantity (wt %)	Reaction extent	α-yield	β-yield
None	–	0.68	11	101
NaF	1	0.49	57	24
CaF$_2$	1	0.60	64	36
AlF$_3$	1	0.65	26	82
AlF$_3$	3	0.49	19	63
AlF$_3$	5	0.41	19	50

Figure 1 The overall fraction of reaction (α) for a silicon compact containing 2 wt% CaF$_2$, and for the reference compact, as a function of time.
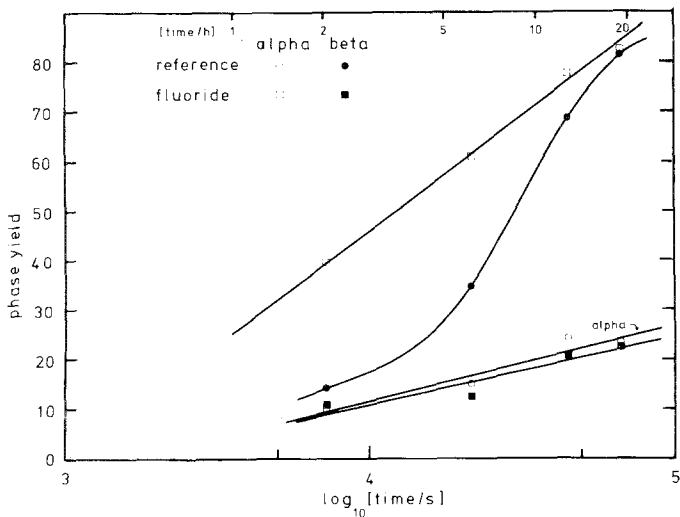
Figure 2 The α- and β-silicon nitride phase yields from the nitridation of a silicon compact containing 2 wt% CaF_2, and from a reference compact, as a function of $\log_{10}$ (time).

ence compacts, are plotted as a function of $\log_{10}$ (time) in Fig. 2. Fig. 3 shows a similar treatment of data for compacts of the silicon powder nitrided alone.

4. Discussion
4.1. Nitridation of silicon alone
The normal nitridation behaviour of the silicon powder used in this study has already been examined in some detail [11]. Fig. 3 shows the characteristic features, the most obvious of which is the marked acceleration in the rate of β-phase formation after a period during which both the α- and the β-phase are formed relatively slowly and at similar rates. The rate of α-phase formation appears to be independent of that of the β-phase. Consequently it has been suggested that the formation of the α-phase of silicon nitride occurs as a

result of reactions involving silicon monoxide, or at surfaces contaminated by oxygen. The unusual pattern of β-phase formation has been attributed to the production and spreading of a liquid silicon–metal alloy, following the elimination of the native silica film on the silicon surfaces. Preferred growth of β-silicon nitride has been observed to be associated with the presence of liquid phases, such as liquid silicon itself at temperatures above $1410°$ C, or silicon alloys with lower melting points, and a direct relationship has been established between the extent of β-phase formation and the iron content of a range of silicon powders [6, 12]. So long as the silica film remains, both the normal nitride nucleation and growth processes, and the reactions of metallic contaminants to form liquid phases, appear to be inhibited.
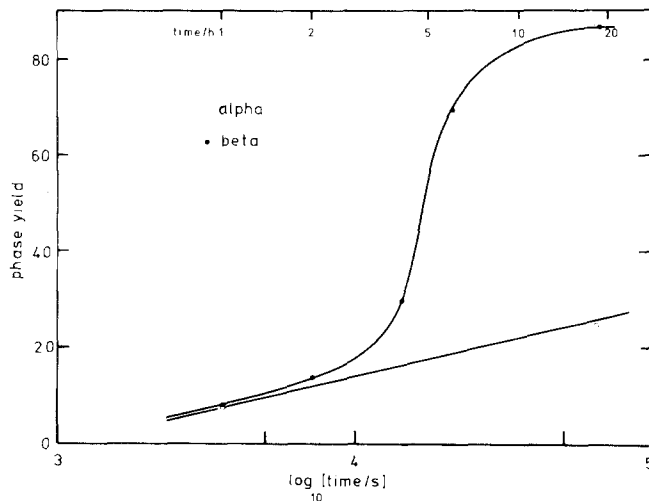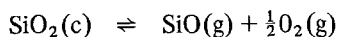
Under standard nitriding conditions the silica

Figure 3 The α- and β-silicon nitride phase yields from the nitridation of a silicon compact alone, as a function of $\log_{10}$ (time).

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film coating all silicon surfaces would be expected to be stable. For the direct evaporation of silica from silicon as silicon monoxide, through the equilibrium:

$$SiO_2(c) \rightleftharpoons SiO(g) + \tfrac{1}{2}O_2(g)$$

the oxygen partial pressure must be less than 5×10^{-9} atm. at $1365°C$ [13]. In practice the nitrogen atmosphere invariably contains water vapour at pressures in the region of 10^{-5} to 10^{-3} atm. (even though the gas may have been pre-dried) and this water will generate oxygen partial pressures well in excess of the critical level. The condition of the system will generally tend to favour therefore the slow passive oxidation of the silicon [14]. Because of the likelihood of the presence of local flaws in the silica film its evaporation will probably be controlled by the equilibrium:

$$SiO_2(c) + Si(c) \rightleftharpoons 2SiO(g)$$
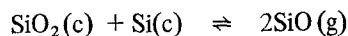
for which K_p is approximately 2.8×10^{-5} atm at $1365°C$, where unhindered evaporation is assumed to occur from those sites where the underlying silicon has been exposed. For a silica film thickness of 3 nm [5] the equivalent volume of silicon monoxide vapour at the equilibrium vapour pressure of 5.3×10^{-3} atm., and $1365°C$, will be of the order of 2500 ml per gramme of silicon powder. Thus for a powder compact of this size in a relatively small reaction chamber and with a gas flow rate of 50 ml min^{-1} some 50 min would be required for the complete evaporation of the silica film and for the exposure of the silicon surface. This calculation assumes however that there is no barrier to the generation of silicon monoxide. If the silica film were disrupted at only a small number of sites the evaporation process could be slowed considerably. Thus the time of 4 h required experimentally for initiation of the fast stage of the β-phase forming reaction does not seem unreasonably long. The slow rates of production of the α- and β-phases before this point is reached must then be assumed to be associated with the relatively small proportion of the total area of the silicon-covered surfaces at which the silicon is accessible.

Removal of the silica film appears to be accelerated in the presence of hydrogen [7, 9], and also by very small amounts of finely dispersed iron [5]. The hydrogen would be capable of effecting evaporation of the silica film through the equilibrium:

$$SiO_2(c) + H_2(g) \rightleftharpoons SiO(g) + H_2O(g)$$
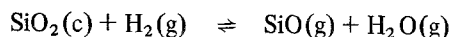
for which K_p at $1365°C$ is approximately 6×10^{-8} atm. The reason for the action of the iron is less immediately obvious and it has been suggested that its function is that of devitrifying the silica, thereby exposing a larger proportion of the silicon-silica interface [6, 10]. In the presence of hydrogen the expected subsequent accelerating action of contaminant iron may not be observed [9], possibly because of the far greater effectiveness of hydrogen in generating suitable surfaces for the rapid nucleation and growth of silicon nitride. The action of even well-dispersed iron must of necessity be a relatively localized, and therefore a less efficient, one in this respect.

4.2. Nitridation in the presence of fluorides

An examination of Table II shows that after 8 h a somewhat ambivalent picture is presented of the action of the three fluorides used in this study. In all cases there is an increase in the amount of α-phase produced compared with that for silicon nitrided alone, markedly so in the case of the sodium and calcium fluorides. The yield of β-phase on the other hand falls by an almost equivalent degree, so that the overall extent of the conversion of silicon to silicon nitride is decreased. It needs to be noted, however, that after 8 h, with this particular powder, onset of the fast β-phase forming stage would normally have occurred. Since this stage of the reaction is primarily controlled by the presence of the metallic impurities, had they not been present the result would have been an overall acceleration due simply to the greater rate of the α-phase production. This fact may help to explain the discrepancies in the literature concerning the action of calcium and barium fluorides. It would seem that in the case of a silicon powder heavily contaminated by metals only a slight change, or even a reduction, in the overall rate of conversion of the silicon over the first few hours would be observed on the addition of the fluoride. In the case of higher purity powders, the fluorides would appear to catalyse the nitridation by accelerating the rate of α-phase formation, and thus to some extent fulfil the general function of a deliberate addition of small quantities of iron catalyst. Whether fluoride additions appear to have an

effect on the initial reaction rate will therefore depend on the purity of the silicon powder in use. In the absence of analyses for the α- and β-silicon nitride phase yields it would be difficult to be sure that the fluorides were not in fact having any effect in cases where no change in reaction rate was detectable.

From the present study it can be seen that the result of the addition of aluminium, sodium and calcium fluorides is qualitatively identical with that of nitridations in the presence of a small percentage of hydrogen [9], in that there is firstly an acceleration of the α-phase forming reaction, and secondly that there is a suppression of the expected later stage accelerating effects of the metallic contaminants. The case of aluminium fluoride appears at first sight to be more complex, in that increased additions do not lead to increased rates of formation of the α-phase. It is probable, however, that this effect is associated with the high vapour pressure of AlF_3 at $1365°$ C (theoretically in excess of 1 atm.) which would be expected to retard the nitriding reaction by hindering the access of nitrogen to the interior of the compact. The importance of the volatility of sodium fluoride was demonstrated by the fact that accelerated α-phase formation could be seen when a silicon powder compact was nitrided merely in the presence of a small quantity of the salt. There was, moreover, a "memory" effect, in that subsequent nitridations following the use of sodium fluoride showed the same α-phase forming tendency, due presumably to the evaporation from the alumina furnace tubing of previously condensed sodium fluoride.

The overall extent of the silicon nitridation reaction as a function of time in the presence of calcium fluoride is shown in Fig. 1, where it can be seen that there is an initially fast rate of reaction, forming an amount of silicon nitride comparable with that formed at a later stage in the cases of the reference sample and the silicon nitrided alone due to the presence of the metallic impurities. Details of the action of calcium fluoride become more clear when the time dependences of the phase-yields are examined. Fig. 2 shows that formation of the α-phase is preferred, and at an initially fast rate. The β-phase forming reaction follows its original course, with no indication of any accelerating effects due to the metallic contaminants. The reference compact on the other hand behaves broadly in the expected way, with

TABLE III Rates of α- and β-silicon nitride formation at constant fraction of overall conversion (0.15)

	$\dfrac{d[\alpha]}{dt}$ $(10^{-3}\ sec^{-1})$	$\dfrac{d[\beta]}{dt}$ $(10^{-3}\ sec^{-1})$
Silicon alone	1.9	1.9
Reference silicon	1.9	1.9
With 2 wt % CaF$_2$	15.9	4.8

the slight difference that the β-phase forming acceleration is delayed. Useful comparisons of the rates of formation of the two phases in the three cases are made at a constant overall fraction of conversion (0.15), and that instantaneous formation rates are presented in Table III. The data show that the action of calcium fluoride addition is to increase the α-phase formation rate at this stage some eight-fold, while the β-phase formation rate is increased by a factor of only about two. This can be compared with the effect of 5% hydrogen at the similar temperature of $1357°$ C, for which the α-phase formation rate of high purity silicon is increased by a factor of approximately 500 at the same overall fraction of conversion, compared with the rate in pure nitrogen. In the presence of amounts of iron (0.28 at %) comparable to those present in the powder used here, the factor is approximately 120 [9].

Our interpretation of the action of these metal fluorides is simply that it accelerates the loss of the native silica film by a mechanism similar to that suggested for finely dispersed iron [10]. That is, by bringing about devitrification and disruption of the film, its evaporation as silicon monoxide is able to occur more readily. More extensive nucleation and faster growth of nitride then become possible. It has already been shown that nitride growth occurs only very slowly at a silicon nitride-silicon interface [15, 16], and the importance of the exposed silicon surface for the growth of nitride elsewhere in the system has also been convincingly demonstrated [5, 17]. Any process which serves to increase the area of free silicon from which silicon can be released either as the vapour, or by surface diffiusion, must therefore have a large effect on the nitridation kinetics.

The required ability of calcium fluoride to cause devitrification of silica is demonstrated in Fig. 4. This shows part of the surface of a polished flat plate of silica which was heated in contact with calcium fluoride powder for 30 min at
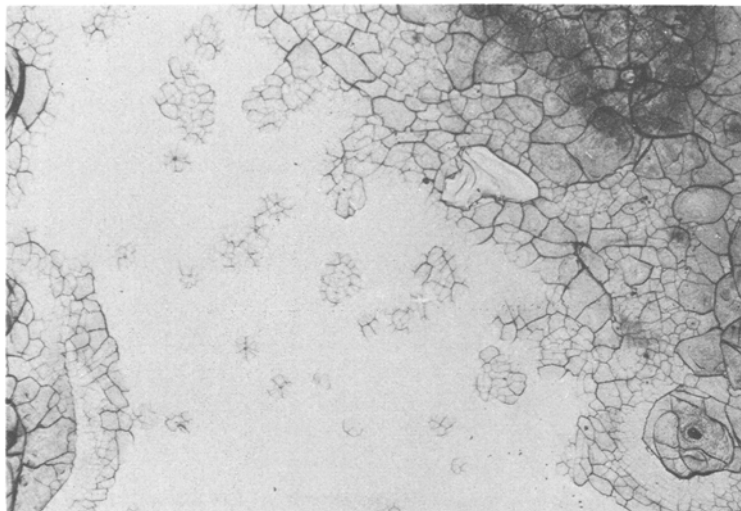
1200° C under nitrogen. A similar silica plate heated alone under these conditions showed no change, nor did a plate located adjacent to the one on which calcium fluoride had been sprinkled. This last point is of interest because of the effects of the presence of calcium fluoride on the reference silicon compacts. The slight delay observed in the onset of the fast β-phase forming stage is similar to that seen when additional silica is incorporated into the system [11]. This suggests that in the case of the reference compact this delay is caused by the release of silicon monoxide from the fluoride-containing compact, which then suppresses the normal evaporation of silica from the silicon surfaces.

It is of some interest that it is predominantly the α-phase of silicon nitride which is formed in the initial stages of the reaction in the presence of calcium fluoride. The arguments for and against the essential presence of oxygen in the crystal lattice of α-silicon nitride, and the possible involvement of oxygen in the formation mechanism of the α-phase, are well documented [11, 18–20]. It is therefore necessary to consider the possibility that fluorine, or fluorine-containing species, are able to play roles similar to those which have been attributed to oxygen.

When it is in contact with the silicon surface, the calcium fluoride will generate silicon tetrafluoride at a partial pressure in the region of 5×10^{-7} atm. at 1365° C through the equilibrium:

$$Si(c) + CaF_2(c) \rightleftharpoons SiF_4(g) + Ca(l)$$
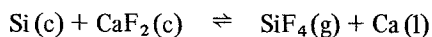
Further reaction of the calcium with traces of oxygen in the silicon compact leading to the eventual formation of calcium silicates would serve to displace the equilibrium to the right. The silicon tetrafluoride itself may enter into an equilibrium with silicon:

$$SiF_4(g) + Si(c) \rightleftharpoons 2SiF_2(g)$$
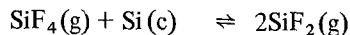
generating the unstable silicon difluoride with an equilibrium partial pressure of 2×10^{-5} atm. Subsequently the silicon difluoride can be nitrided with regeneration of silicon tetrafluoride:

$$6SiF_2(g) + 2N_2(g) \rightleftharpoons Si_3N_4(c) + 3SiF_4(g)$$
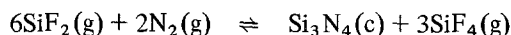
For a partial pressure of SiF_2 of 2×10^{-5} atm., and under 1 atm. nitrogen, the equilibrium partial pressure of SiF_4 is 1.8×10^{-4} atm. The nitridation reaction will proceed provided a sink for SiF_4 exists. Silicon would in fact be adequate in this respect, thus completing the cycle by the regeneration of SiF_2. The arguments applied to oxygen in the context of the formation of the α-phase of silicon nitride could therefore be applied equally to silicon tetrafluoride, and it could also be supposed that fluorine might be incorporated into the α-silicon nitride crystal structure, stabilizing this phase with respect to the β-phase. However, the data obtained from the use of a reference silicon compact in the presence of the calcium fluoride-containing compact provide no evidence for special roles for silicon tetrafluoride such as the ones postulated above. It would be expected that the reference compact

would also be exposed to silicon tetrafluoride vapour at a partial pressure in the region of 5×10^{-7} atm. This is comparable with the partial pressure expected for silicon vapour itself at $1365°$ C (approximately 2×10^{-7} atm.), and it might be anticipated that there would be a tendency towards an increased rate of formation of the α-phase at the expense of the β-phase. This is, however, not seen, and the initial rates of α- and β-phase formation are within experimental error identical with those for silicon nitrided alone (Fig. 3 and Table III). The only change is the much later effect on the yield of β-phase, which is explicable in terms of a retardation in the rate of loss of silicon monoxide from the reference compact, and a consequent delay in the involvement of metal-silicon liquid phases in the nitridation process (Fig. 1).

All these data can therefore be used instead to support the more simple picture discussed by Moulson [21] in which the α-phase is that normally formed as the result of the nitridation of gaseous silicon species (whereas the β-phase may be assumed to result from reactions in the presence of liquid phases). In the present case the action of the metal fluorides would be that of facilitating α-phase formation through the increased flux of silicon vapour from exposed silicon surfaces. Large local concentrations of metallic impurities which would normally act as significant β-phase growth sites must then be assumed to become rapidly covered with dense α-silicon nitride deposits, and thereby rendered ineffective.

4.3. Kinetics of silicon nitridation

The choice of a logarithmic time axis in Figs. 2 and 3 merits comment. This form of presentation was used initially as a convenient method for compressing the time scale so as to allow the quantitative comparison of reaction rates after longer periods of time when the rates were becoming slow [9]. It has since become clear, however, that many sets of data obtained under widely ranging conditions, both for the overall extent of nitridation, and for the separate rates of formation of α- and β-phases, can be fitted to straight lines by this form of treatment. This suggests that the direct logarithmic rate law ("mutually-blocking" pore closure model [22]):

$$\alpha = k \log (at + 1)$$

where α is the fraction of reaction, and a and k are constants, which has already been used in several earlier reports [23-25], has a certain generality for the nitridation reaction in the cases both of silicon bars, and of small powder compacts. The physical model forming the basis for this rate law, as applied to a gas-solid reaction with a solid product, is that reaction takes place only at a limited number of active sites, the number of which decreases with time due to formation of the product, which then effectively blocks access to these sites. Growth sites are also assumed to be capable of interfering with each other, so that the closure of one site affects the activity of neighbouring sites. In some respects the basis for the logarithmic rate law is identical with that for the asymptotic rate law ("self-blocking" pore closure model [22]):

$$\log (1 - \alpha) = -k't$$

previously used for example [17] to fit data points for the early stages of silicon nitridation at reduced pressures. However. attempts to fit appropriate sets of data points from Figs. 1, 2 and 3 to straight lines using the asymptotic rate law were not satisfactory and the reaction rates decreased with time more rapidly than would have been predicted from the initial slopes of the curves. A typical plot is shown in Fig. 5, using values of α corresponding to the ratio $\Delta W_t/66.49$, where ΔW_t is the weight gain observed at time t with 100 units of silicon. Atkinson et al. [17] made different assumptions about the appropriate value for the final weight gain (66.49% here), but in the present case even taking a range of smaller values for the final weight gain failed to provide reasonable fits.

Both of these rate laws are strictly applicable only where the reaction interface area is independent of time. In the general case of a reaction involving a powder, and where the reaction rate is dependent on the reactant surface area, corrections may need to be applied to take account of the decrease in area with time. If the particles are assumed to be spheres which diminish in size with extent of reaction due to removal of material then:

$$\frac{A_0 - A_t}{A_0} = (1 - \alpha)^{2/3}$$

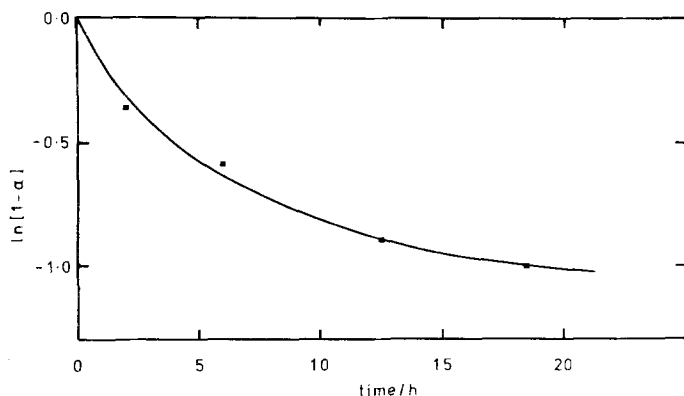where A_0 and A_t are the surface areas at times

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Figure 5 A test of the asymptotic rate law, for the extent of reaction as a function of time for silicon powder containing 2 wt% CaF_2.

0 and t, and α is the fraction of material reacted.

In the case of reaction models described by the logarithmic and asymptotic rate laws, not only would the number of active sites per unit area diminish with time due to blockage by the product, but in addition the area available to the active sites would also diminish. Thus it must be assumed either that the site density increases, or that some sites are eliminated in proportion to the decreased surface area. In the latter case, the correction factor to be applied to take account of a change in area would not lead to significant departures from the logarithmic or asymptotic rate laws until the value of α was about 0.6, so that for small extents of reaction data obtained from powders would still be fitted reasonably well by these equations.

There is evidence that the reaction rate for the formation of the α-phase of silicon nitride is approximately proportional to the initial surface area of the silicon powder [12]. On the other hand there is no evidence that the rate of the nitridation reaction does depend on the instantaneous surface area of the unreacted silicon particles. Indeed the good fitting of data points to the logarithmic rate law even for relatively large values of α suggests that it might not in fact do so. It may, then, be supposed that the reaction rate is controlled at all times by the active density at the original surface of the silicon particle. Because of the volatility of the reactive species in this system, and the slowness of any reaction at the silicon-silicon nitride interface, once the silicon nitride growth patterns are established using these surface sites the reaction rate will thereafter continue to be controlled by them. The active sites will then consist of channels in the silicon nitride, having their origin in flaws in the native silica film at the silicon surface, through which silicon vapour can diffuse outwards with the creation of the large

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voids often seen at the silicon-silicon nitride interface [15–17], or nitrogen can diffuse inwards leading to internal nitridation of the silicon at these void surfaces. As implied by the rate laws, the only factor leading to a decrease in $d[\alpha]/dt$ with time will then be a progressive sealing of these channels either by externally, or by internally, deposited nitride. Certainly the evidence for the formation of voids underlying the original silicon surfaces, and the linking of these voids to form larger cavities, indicates that if there were a dependence of the reaction rate on the instantaneous silicon surface area, then the effect on the nitridation rate would be a complex one, and not readily amenable to precise quantitative treatment. That the rate law controlling process is associated with the behaviour of each individual particle surface in a powder compact, and is not some function of the particle size distribution within the compact, is shown by the fact that the direct logarithmic rate law can be applied equally to compacts of classified silicon powders of narrow particle size range [26]. The above model is shown schematically in Fig. 6.

The different kinetic behaviour shown by this study compared with that of Atkinson *et al.* [17], in that the reduced pressure data could be fitted to the asymptotic rate law, whereas the data obtained at 1 atm. pressure could not, may be explicable in terms of the decreased density of growth sites observed during nitridations at lower pressures, and hence a greatly reduced probability that these would interact in the way required by the "mutually-blocking" pore closure model. On the other hand there may be other differences between the two systems, because of the apparently rapid approach to a zero reaction rate at a relatively small fraction of conversion when reduced nitrogen partial pressures are used. This suggests that
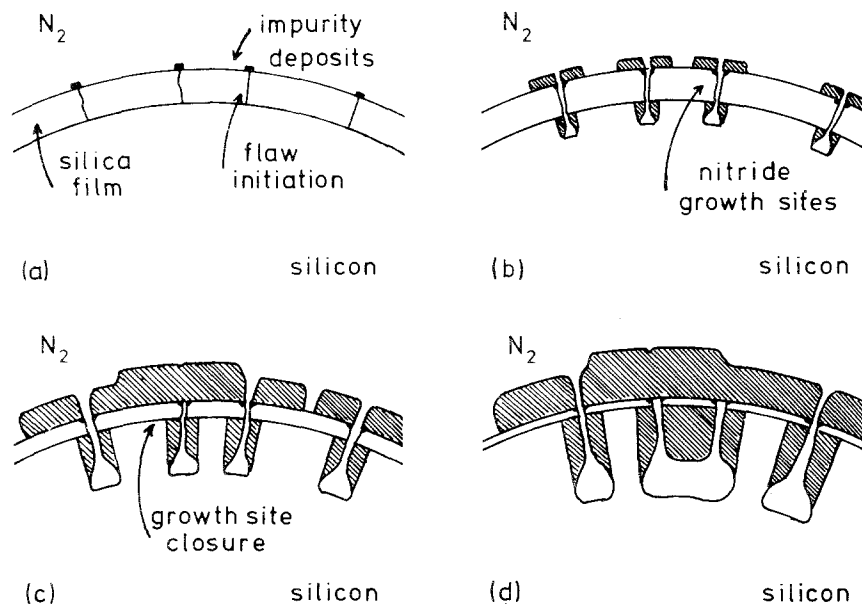
Figure 6 Schematic representation of the pore-closure model (after [17]) for the initiation and development of silicon nitride growth at the surface of a silicon particle. (a) Impurity deposits leading to localized damage to a protective silica film. (b) Development of nitride growth sites at points where evaporation of the silica film has occurred. (c) Internal pore development within the silicon, due to an outward flux of silicon, and the extensive formation of silicon nitride around these growth sites leading to site closure. (d) Continuing silicon nitride formation and associated growth site closure, producing a reduction in silicon nitride growth rate describable in terms of a logarthmic rate law.

under such conditions the silicon nitride has a different texture, and is able to block the growth sites more efficiently. Both rate laws nonetheless appear to be entirely consistent with the model developed for the silicon nitridation process on the basis of the evidence obtained from optical and scanning electron microscopy of nitride growth patterns on silicon single crystal slices, and on silicon grains in powder compacts. They are also consistent with the view that the initial number of sites at which nitride can be nucleated is limited by the presence of the silica film, and that the number of such sites is increased in proportion as the integrity of this film is destroyed.

This aspect of the silicon nitridation reaction is one which needs to be developed further by careful attention to the details of silicon nitridation rates and phase yields at both very short, and very long, nitridation times, under conditions of controlled material purity and particle size, and with a wide range of nitrogen partial pressures. On the basis of the above discussion it might be predicted that a change-over from a logarithmic to an asymptotic rate law should be seen at a characteristic pressure, dependent on temperature, as the nitrogen partial pressure in the system is reduced.

A wider range of accurate data is therefore needed in order to establish more precisely the origin of the growth nuclei, and the effects of nuclei density on the kinetic behaviour of the silicon.

5. Conclusions

It appears that metal fluorides as a class accelerate the initiation of the silicon nitridation reaction by a devitrifying action on a protective silica film. They thus have the effect of increasing the effective surface area of silicon at which nitridation can occur, or from which silicon can be released to form nitride elsewhere. In this respect the action of the fluorides is identical with that of finely dispersed transition metals. Any material known to be capable of devitrifying silica at high temperature should therefore also be capable of accelerating the nitridation reaction. The predominant phase produced at an accelerated rate in the early stages of the reaction is α-silicon nitride, in accordance with the suggestion that this is the normal product of the nitridation of gaseous silicon species.

The observation that data from nitridations carried out under nitrogen partial pressures in the region of 1 atm. can be fitted to the logarithmic

rate law is consistent with the model developed for the nucleation and growth of silicon nitride on silicon surfaces, and with the observed importance of the native silica film on these surfaces.

Acknowledgements

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