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A mechanism for the nitridation of Fe-contaminated silicon

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The influence of iron impurity on both the oxidation and nitridation of high purity silicon has been investigated. It is shown that iron is effective in rapidly removing the protective silica film which normally covers silicon. Experimental evidence suggests that the removal is achieved by iron-induced devitrification and disruption of the silica, thus allowing the SiO (g) generated by the Si/SiO_2 interface reaction to escape. During the nitridation of iron-contaminated silicon powder compacts it is found that iron significantly enhances the extent of reaction for contamination levels of <1000 p.p.m. Fe (by weight). Above this level there is a decrease in the rate of formation of extra nitride. At all levels of contamination the percentage of silicon converted to β-Si_3N_4 was observed to be directly proportional to the iron concentration, and it is shown that this β-growth occurs within an $FeSi_x$ liquid phase. The possible implications of the findings for the optimization of strength of reaction-bonded silicon nitride are briefly discussed.

1. Introduction

Reaction-bonded silicon nitride remains a promising high-temperature engineering material [1] and research into the mechanism of the reaction-bonding process continues. As stressed in previous publications [2, 3], the course of the reaction is sensitive both to the presence of impurities in the system and to process parameters. It is neglect of control of the many variables which has inevitably led to there being only small return, in terms of understanding, for the considerable research effort.

The need to work towards an understanding of the reactions occurring during nitridation of a "commercial" silicon powder (typically approximately 98% Si; 0.9 wt% Fe), by separation of the effects of the many variables involved, was recognized by Atkinson *et al.* [2], and they were successful in elucidating the mechanism by which spectrographically pure silicon nitrided. According to their model, the initial stage of the reaction involves the nucleation and growth of nitride, during which the kinetics are linear with time. After the initial stage, nitridation proceeds at a decreasing rate determined by vapour transport through gradually blocking channels in the developing nitride film, the rate being effectively "zero" when a nearly complete film is developed. The extreme sensitivity of the kinetics to the presence of transition elements was also confirmed [3].

The reaction-accelerating effect of iron, the most commonly encountered impurity in commercial grade silicon powder, has long been recognized [4], and Messier and Wong [5] proposed that it is related to the formation of $FeSi_x$ phases, liquid at nitriding temperatures. The association of iron-enhanced nitridation with $FeSi_x$ liquid was further strengthened by Atkinson [6] and Leake [7] who found there was no Fe-induced extra nitridation, in powders of otherwise high purity, at reaction temperatures below 1200° C, approximately the minimum Fe–Si solidus temperature. A similar situation obtained for chromium-contaminated silicon [7].

Atkinson *et al.* [3, 6] invariably observed sigmoidal-type kinetics for the nitridation of Fe-contaminated silicon of otherwise high purity, as shown in the example in Fig. 1. The initial part, or "induction period", of the kinetics is associated with the removal, as SiO(g), of the reaction-inhibiting surface oxide film on silicon. This loss

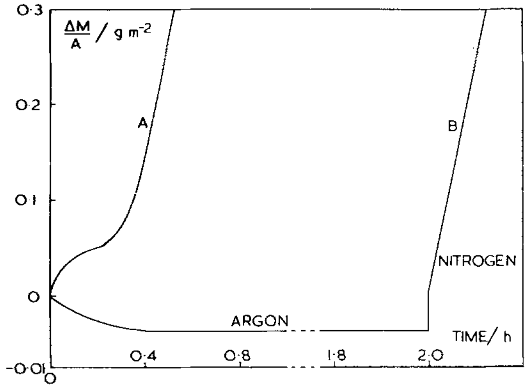

Figure 1 Curve A: Nitridation kinetics; curve B: Oxide film removal and subsequent nitridation. (Si + 2000 p.p.m. Fe at 1370° C). After Atkinson and Moulson [3]. Note different scale of $\Delta M/A < 0$ ($\Delta M/A$ = weight gain per unit total surface area).

of oxide is confirmed by heating a similar sample in argon where the weight loss observed corresponds to the weight of surface oxide in the sample (Fig. 1). An estimate [6] of the activation enthalpy of the oxide-removal mechanism, made from the temperature dependence of the induction time, lent support to the view that oxide removal occurred by the reaction:

$$\mathrm{Si\,(s) + SiO_2\,(s) = 2SiO\,(g)} \qquad (1)$$

The mechanism of removal was, however, not investigated.

As far as the authors are aware, no consensus of opinion exists regarding the effect Fe has on the relative amounts of the α and β-Si_3N_4 phases produced by nitridation. It has been variously reported to have no effect [5, 6] to increase the proportion of the β-phase of silicon nitride [8, 9] and in one case to increase the proportion of α-Si_3N_4 [10]. As in the case of the conflicting kinetics data, it was thought likely that the confusion arose through a lack of appreciation of the effects of other impurities and of process variables.

It was the intention that the present study would detail the mechanism by which iron removes the inhibiting surface oxide layer on silicon and would explain its effect on both the phase composition and extent of subsequent nitride growth. A detailed explanation of the mechanism of surface oxide removal has been presented elsewhere [11] and only a summary is given here.

2. Experimental

2.1. Materials

The silicon powder used throughout the study was spectrographically pure and of particle size $< 53\,\mu$m, prepared from undoped, semiconductor-grade silicon ingots, in the manner described by Atkinson *et al.* [2]. Deliberate contamination by iron at levels of between 50 and 5000 p.p.m.* Fe was achieved by mixing the silicon with a solution of iron nitrate in alcohol, the alcohol then being evaporated away. Cylindrical compacts, typically of 1.5 g, were formed by isostatic pressing at 200 MNm^{-2}, in the absence of a binder.

In a subsidiary experiment, vitreous silica slabs ("Vitreosil", Thermal Syndicate Ltd.) were surface-contaminated with iron by vacuum evaporation of metallic iron wire (B.D.H. Chemicals Ltd.) from a spiral tungsten filament.

2.2. Effect of iron on the kinetics of oxidation

The oxidation kinetics of pure silicon were studied by thermogravimetry using apparatus described elsewhere [2, 3]. Samples of approximately 1.5 g of pure loose silicon powder were placed in an alumina ("Purox", Morgan Refractories Ltd.) crucible and oxidized at 1370° C in air at various pressures. In a typical run the sample was removed from the TG balance when the "zero-rate" region of the parabolic oxidation kinetics curve was approached. Approximately 3000 p.p.m. iron was then added to the partially oxidized sample which was returned to the balance and oxidized for a further period under the same conditions.

The Fe-contaminated vitreous silica slabs were heated in the TG balance under normal nitriding conditions ($P_{N_2} = 1$ bar; $P_{O_2} \sim 10^{-5}$ bar; 1150 to 1400° C).

2.3. Effect of iron on the nitriding reaction

The effects of iron contamination on both the phase composition and reaction extent were investigated. Attention was given to the purity of both the reaction environment and nitriding gas. To reduce the risk of contamination of the sample by the furnace parts [12, 13], the alumina crucible in which the compacts were to be nitrided was lined with high purity molybdenum foil; the sample also rested on the edge of a coiled molybdenum strip so as to incur minimum solid contact. Re-

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*All concentrations are p.p.m. by weight.

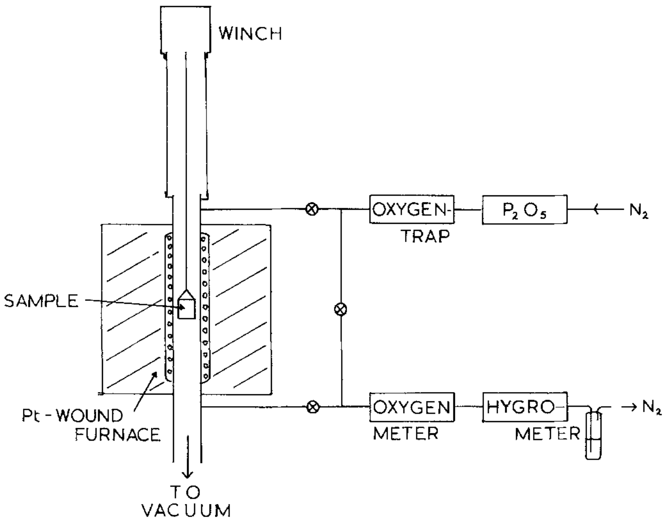

Figure 2 Nitriding furnace and gas flow system.

actions were carried out at 1350° C in flowing nitrogen ("White Spot", British Oxygen Co., 1 atm.) in which O_2 and H_2O concentration were lowered by manganous oxide and phosphorus pentoxide traps. Measured levels of oxygen (home-made zirconia O_2-meter) and water vapour (electrolytic hygrometer, SEI Ltd., Salford, UK) after this treatment were respectively $\sim 10^{-6}$ v.p.m.* and ~ 1 v.p.m. The oxygen potential in the reaction zone was further reduced by the presence of a zirconium foil "oxygen-getter" within the crucible and adjacent to the sample. Because the specimens were contained in a "closed" crucible, the reported effects [14] on the nitridation reaction of flowing nitrogen gas were not considered, the samples being exposed to constant excess of static nitrogen.

Nitridation reactions were carried out in a vertical, platinum-wound furnace which, together with the gas supply system, is shown diagrammatically in Fig. 2. The nitridation of uncontaminated silicon was preceded by a vacuum "deoxidation" treatment, as it was known that the reaction-inhibiting native oxide layer can be removed by heating at nitriding temperatures (1350° C) in vacuo (10^{-7} bar) [6, 15]. The samples were given a 15 min vacuum pre-treatment in the reaction zone prior to admission of N_2. Nitridation of Fe-contaminated samples was carried out without vacuum pre-treatment.

2.4. Product analysis

The reaction products were examined using X-ray diffractometry and reflected light microscopy. The α/β-Si_3N_4 ratio was determined from the ratio of the β_{210} and α_{102} X-ray diffraction peak heights, in a manner described by Weston [16]. Because no deposits formed in the cool parts of the apparatus, material loss from the sample by vapour transport was considered to be negligible; the reaction extents were, therefore, determined solely by weight gain.

3. Results

3.1. The effect of iron on the oxidation kinetics

The effect of iron on the kinetics of oxidation of loose, pure silicon powder in air at various pres-

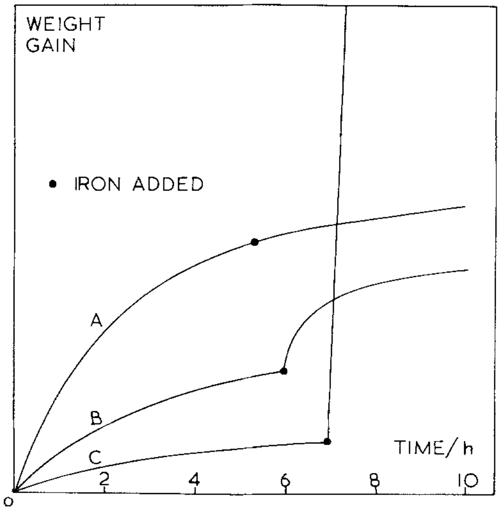

Figure 3 Pressure dependence in the oxidation kinetics of iron-contaminated silicon. Curve A: $P_{O_2} > 15$ Torr; curve B: 15 Torr $> P_{O_2} > 4$ Torr; curve C: $P_{O_2} < 4$ Torr.

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*v.p.m. = volumes per million.

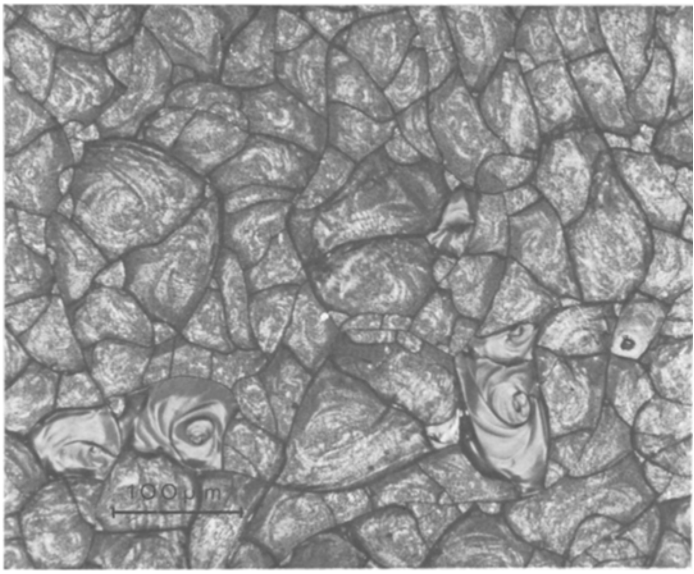

Figure 4 The disruption of silica glass by iron.

sures (equivalent P_{O_2} : 0.4, 2, 3, 5, 7, 12, 20, 152 Torr) showed a strong oxygen pressure dependence as explained below and shown schematically in Fig. 3. It was found that:

(i) Below $P_{O_2} \approx 4$ Torr, the oxidation rate was markedly accelerated by additions of iron. After reaction times of 10 h the crucible was found to contain silicon powder at the bottom, the colour of which had changed from blue/green to grey; these colours are characteristic of oxidized and unoxidized powders respectively. The top of the crucible was closed by a crust of α-cristobalite, deposits of which were also found on the suspension supporting the crucible and in other parts of the reaction system.

(ii) At $\sim 4 < P_{O_2} <\sim 15$ Torr, the addition of iron was found to produce a sudden increase in weight gain. This effect was short-lived and decreased with increasing pressure. Analysis of the reaction product showed that the silicon particles were coated with a layer of α-cristobalite. No other reaction product was formed.

(iii) At $P_{O_2} >\sim 15$ Torr the addition of iron was found to have no measurable effect on the reaction kinetics. Analysis showed the reaction product to be the same as in (ii) above.

3.2. Silica glass contaminated with Fe

Specimens of iron-contaminated vitreous silica slabs, heated in nitrogen at 1150° C and at 50° C increments to 1400° C, showed clear evidence of devitrification. In all cases optical examination of the contaminated surfaces showed them to be extensively microcracked (Fig. 4) and observation under crossed polars showed the presence of small anisotropic crystals. X-ray diffraction confirmed the presence of α-cristobalite, the normal devitrification product from vitreous silica [17].

The experiments were extended to include vitreous silica contaminated with various metal powders (Fe, Ni, Ta and Al) and the results, after heating in nitrogen (P_{N_2} = 1 bar) for 2 h at 1370° C, were as follows.

Ni and Fe contamination led to both devitrification and disruption. The iron-contaminated sample showed evidence of melt formation, as would be expected under the above condition [18]. The Ta and Al contamination left the silica glass largely unaffected; no devitrification was seen and X-ray analysis showed both the Ta and Al to have nitrided. Vitreous silica which was uncontaminated remained stable under the above experimental conditions.

3.3. The effect of iron on the nitridation of pure silicon

The kinetics of formation of the α- and β-phases of silicon nitride during nitridation of silicon + 1000 p.p.m. Fe powder compacts were investigated. The effect of Fe additions to the silicon on both the reaction extent and phase composition of the product was also studied. The results are summarized in Table I and expressed graphically in Figs. 5 and 6.

In order to study the way in which Si_3N_4 growth occurs in the presence of iron, pure silicon

TABLE I Product of the nitridation at 1350° C of Fe-contaminated silicon

Sample no.	Time (h)	Fe (p.p.m. by weight)	% Reaction	α (wt %)	β (wt %)	β-yield (%)*
1	0.75	1000	13.2	87	13	1.72
2	2.0	1000	24.1	86	14	3.37
3	5.0	1000	32.5	86	14	4.55
4	10.0	1000	37.7	85	15	5.66
5	10.0	0	11.4	70	30	3.42
6	10.0	55	30.3	88	12	3.64
7	10.0	200	31.1	87	13	4.04
8	10.0	500	34.0	86	14	4.76
9	10.0	2500	40.5	81	19	7.89
10	10.0	5000	47.2	75	25	11.80

*The "β-yield" for the reactions is defined as the product of the percentage of the silicon converted and the fraction of the nitride which is of the β-Si_3N_4 phase; this represents the percentage of silicon converted to β-Si_3N_4. The α-yield is defined similarly.

powder of particle size $\leqslant 100\,\mu m$ was wet-mixed with 8 wt % iron powder. In this way local regions of high iron concentration were produced within the silicon compact, the large silicon particle size facilitating subsequent microscopical examination. X-ray analysis of the reacted compact (10 h at 1350° C) revealed silicon, iron disilicide and α- and β-Si_3N_4, the proportion of β-Si_3N_4 being high (63 wt %).

Reflected light microscopy of a polished section through the reacted compact showed a yellow second phase within the silicon grains into which large, well-faceted crystals of silicon nitride were growing (Fig. 7). Electron probe microanalysis revealed the second phase to be of approximate composition $FeSi_2$. Nitride growth was in all cases seen to be associated with the $FeSi_2$ second phase which, at temperatures greater than 1212° C [19], will be liquid.

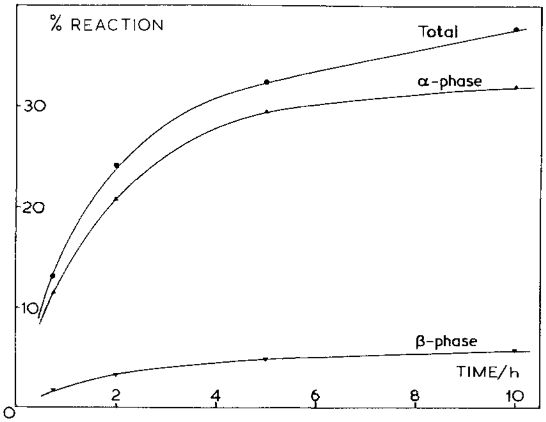

Figure 5 The kinetics of formation of α- and β-Si_3N_4 from Fe-contaminated silicon (1000 p.p.m) at 1350° C.

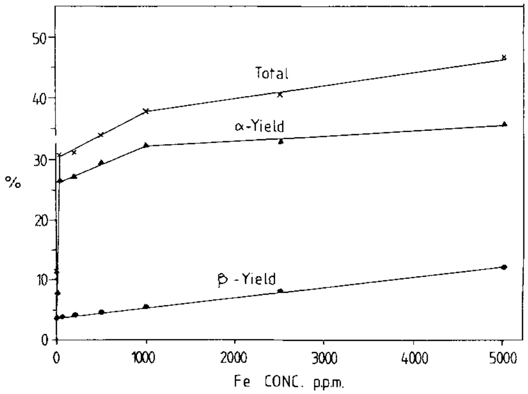

Figure 6 The dependence of reaction extent and phase composition on Fe concentration after 10 h nitridation at 1350° C. ● β-yield; ▲ α-yield; × % reaction.

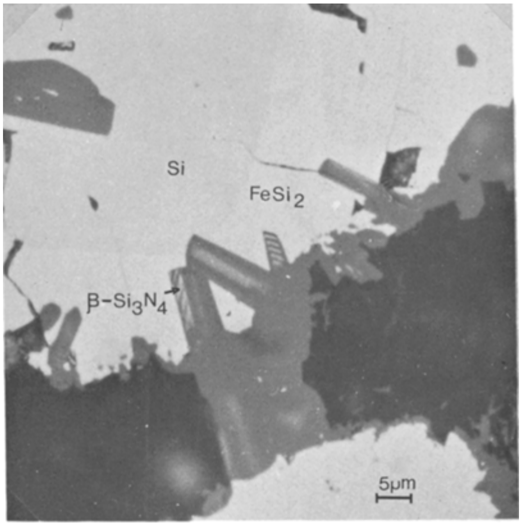

Figure 7 Growth of β-Si_3N_4 within an $FeSi_2$ liquid phase; the β-Si_3N_4 crystals showing faceting and optical interference ("ladder" effect), erroneously regarded as a particular growth morphology of Si_3N_4 [44].

4. Discussion

4.1. Effect of iron at the initial stage of nitridation: Removal of the oxide film

The study of the effect of iron on the oxidation kinetics of pure silicon showed there to be a marked oxygen pressure dependence which may be interpreted in terms of the "passive" and "active" oxidation of silicon.

The oxidation kinetics of iron-free silicon were parabolic and showed a slight oxygen pressure dependence, as has been found previously [20], reaction occurring by diffusion of the oxidizing species through a protective oxide film; that is, "passive" oxidation. The coherent silica film will remain stable at oxygen pressures greater than $\sim 10^{-8}$ bar at 1370° C.

The addition of iron had no effect on the oxidation kinetics at high oxygen pressures. However, as the oxygen pressure was reduced, enhanced oxidation occurred and, below a critical oxygen pressure ($\sim$ 4 Torr), the oxidation rates were two to three orders of magnitude greater than the "passive" rates (Fig. 3 curve C). At these low pressures the reaction product was formed remote from the silicon, which no longer carried an oxide film. This indicated a change from gas–solid to vapour phase reaction. The pressure at which the transition occurred was close to that predicted by Wagner [21] for the silicon active/passive oxidation transition.

"Active" oxidation occurs by reaction of oxygen with the silicon surface to form SiO(g), which then diffuses away. Such a reaction requires an oxide-free surface and it follows, therefore, that in the present case, iron is capable of exposing the underlying silicon to the reacting gas. It is postulated that devitrification of the surface silica by iron reduces its adhesion to the underlying silicon, the SiO(g) formed at the Si/SiO_2 interface, according to Equation 1 and in agreement with Atkinson's work [6], then escaping through fissures in the disrupted silica film. This reaction will continue until the silica film is removed completely, oxygen within the system at pressures below $\sim$4 Torr then forming further SiO(g) and the silicon surface remaining free of solid oxide, in accordance with the Wagner model. SiO(g) formed in this manner during the oxidation experiments was further oxidized remote from the sample to α-cristobalite, which is the expected reaction product of the re-oxidation of SiO(g) in the vapour phase at temperatures in the region of 1400° C [22].

The enhanced oxidation rate observed at P_{O_2} greater than the critical pressure may have been the result of a recurrent "exposure-re-oxidation" process. Alternatively, after exposure of the underlying silicon, a non-protective film may have formed of the type suggested by Hinze and Graham [23] when a second-stage, "active" oxidation, and consequently a second critical oxygen pressure, was said to occur.

It may be significant that the metallic contaminants which have been shown to accelerate the nitridation reaction (Fe, Ni [3]) were found to devitrify silica under the nitriding conditions, whereas those which were found to have no effect on nitridation kinetics (Al, Ta) did not. Supporting evidence for the concept of devitrification as the mechanism by which iron causes the removal of the reaction-inhibiting silica layer is found in the work of Ainger [24] who demonstrated that silica films on silicon devitrified readily in the presence of suitable nucleating agents.

4.2. Effect of iron during the nitritation reaction: Enhancement of extra nitride growth and its phase composition

The kinetics of formation of α- and β-Si_3N_4 (Fig. 5) showed both phases to form uniformly within the reaction times studied, in such a way that the α/β ratio was independent of time. It was for this reason that in the subsequent experiments only the α/β ratio after 10 h reaction was determined.

Small additions of Fe (55 p.p.m.) produced almost a three-fold increase in reaction extent compared to that observed for the pure powder compacts (Table I); the extra nitride grown beyond the initial stage varied linearly with further Fe additions. The rate of formation of the extra nitride grown decreased with Fe addition beyond 1000 p.p.m., and Fig. 6 shows that this is a result of a fall-off in the rate of growth of α-Si_3N_4, since the β-growth remained linear with Fe addition.

In the case of the heavily contaminated sample, the β-growth was seen to occur within an $FeSi_2$ liquid phase (Fig. 7), the hexagonal growth habit being typical of the β-growth morphology observed by other workers in the nitridation of commercial silicon powders [25, 26]. The growth of β-Si_3N_4 has been known to be favoured by the presence of liquid, Evans and Davidge [27], for example, finding that high β-yields result when nitridation occurs above the melting point of silicon. An association between β-growth and liquid phase is also an essential feature of current views concerning the conversion of α- to β-Si_3N_4 [28, 29].

In contrast, the formation of α-Si_3N_4 is associated entirely with vapour phase reactions, pyrolytically deposited crystalline silicon nitride being invariably of the α-form [30].

As a result of the present study it is proposed that the enhancement by Fe impurity of the formation of both α- and β-Si_3N_4 is solely dependent upon the presence of an Fe/Si liquid phase.

It is suggested that α-Si_3N_4 forms in the vapour phase above the iron–silicon liquid. It has been shown by Atkinson *et al.* [2] that at $P_{N_2} = 1$ bar, uncontaminated silicon is rapidly covered by a nitride film which effectively prevents further reaction. The presence of an iron–silicon liquid, which has been shown to wet silicon nitride [31], would provide an effective route via which silicon could move from the solid to the vapour phase.

It is not surprising then that additions of even low levels of iron lead to a dramatic increase in α-formation, the presence of the Fe/Si liquid preventing the formation of the coherent reaction-inhibiting nitride layer and allowing vaporization to continue. The amount of silicon vapour generated would be expected to be proportional to the surface area of the liquid; hence at low levels of contamination the rate of the α-forming reaction would be proportional to iron concentration. As iron contamination is increased, a stage would be reached where further iron only produces a deeper liquid "pool", the exposed surface area remaining sensibly constant. This might be the cause of the observed fall-off in the rate of extra α-formation with Fe at high concentrations (Fig. 6).

In recent work the authors have found the β-yield to be neither total nitrogen nor partial nitrogen pressure dependent. This suggests that the rate of β-Si_3N_4 grown in the Fe-contaminated samples is controlled by the solubility and diffusivity of nitrogen in the $FeSi_x$ liquid [32, 33]. The extent of β-growth would then, as demonstrated in Fig. 6, be expected to increase linearly with liquid content, and, in consequence, with Fe content. The 22% volume increase required for conversion of Si to Si_3N_4 can be accommodated during the β-growth by a combination of liquid displacement and solution of solid silicon in liquid, with its continuous vaporization to form the α-Si_3N_4.

An earlier suggestion [2] that Fe-induced "whisker" growth influenced kinetics through its interference with the development of a coherent, reaction-inhibiting nitride film, is no longer entertained by the authors.

The growth mechanism for β-Si_3N_4 suggested recently by Jennings and Richman [26, 34] is not viable. The suggested mechanism involved solid state diffusion of nitrogen through channels which exist along the *c*-axis of β-Si_3N_4 and was based in part on a model suggested by Atkinson *et al.* [35]. This model involved solid state diffusion of nitrogen in Si_3N_4, accompanied by vacancy condensation in Si, as the steps in the formation of a coherent nitride film. However, in a later, more detailed study of the nitridation of spectrographically pure silicon, which is described briefly in the Introduction, Atkinson *et al.* [2] determined "solid-state diffusion to play no significant part".

Furthermore, it is the experience of the authors and also of Atkinson in previous studies, and where the reaction temperatures were below the melting point of Si, that the well facted β-growth (Fig. 7) occurs only in the presence of those cation impurities which would lead to liquid formation. It is significant too that the conditions found by Jennings and Richman [26] to favour such β-growth were high reaction temperatures (> 1450° C), high impurity content (~ 12 wt% cation impurity) and rapid heating rate, all of

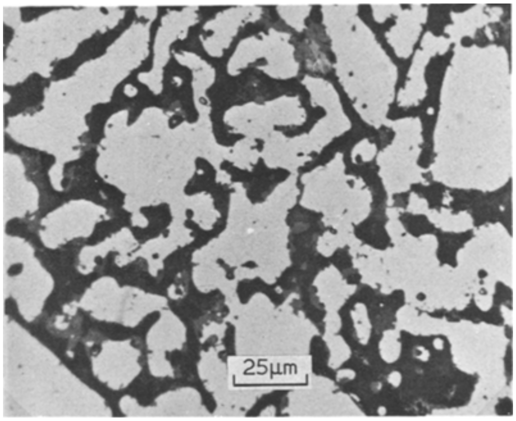

Figure 8 Microstructure of iron-free silicon nitrided for 10 h.

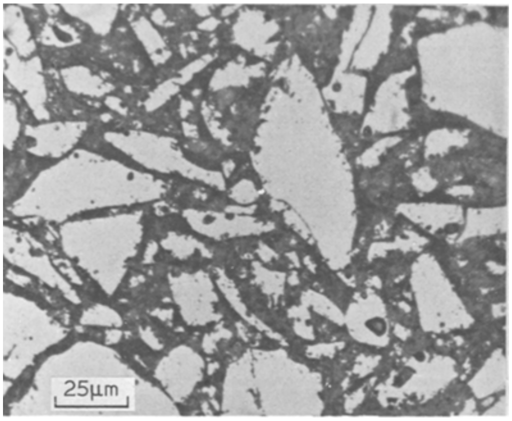

Figure 9 Microstructure of iron-contaminated (55 p.p.m.) silicon nitrided for 10 h.

which contribute to the formation of liquid phase, in the latter case as a result of the exothermic nature of the reaction.

Fe, in addition to influencing the reaction rate extent, and the product phase composition, was also seen to have a hitherto unreported effect on the microstructure of the partially nitrided compacts. Sintering of the silicon, which was found to be a feature of iron-free compacts (Fig.8), was totally suppressed by the presence of even 55 p.p.m. Fe (Fig. 9). It is thought unlikely that this sintering was solely as a result of a 15 min vacuum pre-treatment, as similar effects, which can be related directly to the presence of Fe, have been observed by Arundale [36] during the argon-sintering of compacts. Arundale and Moulson [37] also observed that local melting of iron-rich zones produced voids by penetration of a liquid phase into the surrounding matrix, local regions (~ 600 μm) of inhomogeneity subsequently developing.

A proposed model for the nitridation of iron-contaminated silicon is shown schematically in Fig. 10.

4.3. Implications of the study to control of mechanical properties of RBSN

In the present study high purity silicon has been used, contaminated in a controlled way with iron; also the reactions have been carried out in carefully controlled conditions of temperature and nitriding atmosphere. In these respects the situation differs from that encountered in the commercial production of reaction-bonded silicon nitride, and the latter certainly represents a very much more

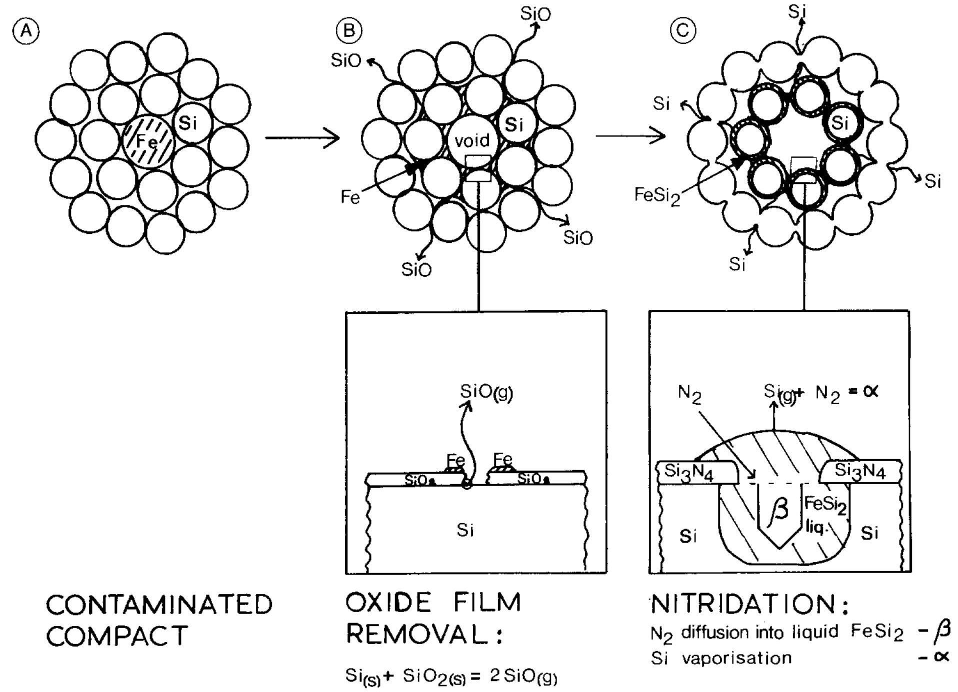

Figure 10 A suggested mechanism for the enhancement by iron-impurity of the silicon nitridation reaction. (A) Silicon compact contaminated by particulate iron. (B) Initial stages of reaction; void formation and oxide film removal, SiO (g) forming α-Si_3N_4 whiskers. (C) Nitridation; $FeSi_2$ liquid enhancing the formation of both α- and β-Si_3N_4; silicon sintering in iron-free regions.

complex system. Nevertheless, the authors believe that the observations made below are relevant to the production of commercial material and to development work aimed at optimizing its mechanical properties.

It is significant that whisker growth has not been a feature of the general microstructures observed during the course of the present study, although during the initial stages of the reaction, α-Si_3N_4 whiskers did form as a result of the nitridation of SiO(g), as has been observed by other workers [38, 39]; this growth, which formed on the external surfaces of the compacts, was absent when the native oxide film had been evaporated under vacuum as SiO(g), prior to admission of N_2.

The general observations, therefore, support the views expressed by Longland and Moulson [40] that the strength of RBSN derives from the formation of massive, vapour-deposited α-Si_3N_4 and that whisker material accounts for a minor part of the product of the reaction. Such a view is in accord with general experience in the field of gas–solid reactions [41].

Although Fe is beneficial in enhancing this α-forming reaction, as the present study has shown, other possible effects it might have on the developing microstructure deserve consideration:

(i) Fe suppresses the sintering of silicon particles during argon-sintering or nitridation of the silicon powder compact.

(ii) Large defects can be caused by the melting of particulate iron [37]. In this context it is noted that the minimum temperature at which Fe/Si liquid will form (~ 1212° C) may be lowered considerably in the commercial situation, where aluminium impurity is also present. It is estimated that in local regions of high Al-contamination the liquidus temperature might readily be as low as 1000° C [42].

(iii) The growth of β-Si_3N_4 into $FeSi_x$ liquid would not seem to be a significant contributor to the development of the mechanical strength of RBSN, the process serving simply to convert, *in situ*, Si to Si_3N_4.

It is suggested, therefore, that although Fe accelerates the reactions to form RBSN, it might also have a deleterious effect upon the mechanical strength of the ceramic. Such a view gains support from the observation of Elias *et al.* [43] that low strengths are invariably associated with high β-Si_3N_4 contents, which are now shown to be dependent upon Fe-impurity.

5. Conclusions

(1) At low oxygen pressures ($P_{O_2} < 4$ Torr at 1370° C) Fe induces a transition from conditions of "passive" to those of "active" oxidation. The transition is achieved by devitrification and disruption of the protective silica film allowing the SiO(g) generated at the Si/SiO_2 interface to escape, the reaction continuing until the silica film is removed completely.

(2) In the nitridation of silicon, even very low levels of Fe-impurity significantly enhance the nitridation reaction. The initial stages involve the removal of a protective silica film in the manner described in (1) above. The exposed silicon surface remains free of solid oxide during nitridation at oxygen partial pressures of up to ~ 4 Torr. It is proposed that Fe then enhances the formation of both α- and β-Si_3N_4 from $FeSi_x$ melt sites as follows: α-Si_3N_4 forms in the vapour phase by the nitridation of Si(g) which vaporizes from $FeSi_x$ (l), the uncontaminated regions of Si(s) surface being rapidly covered by a nitride film effectively preventing further reaction. The extent of the formation of α-Si_3N_4 would be expected to depend upon the exposed surface area of the $FeSi_x$ (l) which, it is suggested, is proportional to Fe content up to approximately 1000 p.p.m.

β-Si_3N_4 precipitates within the $FeSi_x$ liquid and it is thought likely that the rate of growth is determined by the solubility and diffusivity of N_2 in $FeSi_x$ (l). Such β-growth is directly proportional to the amount of liquid, and hence, iron, content.

(3) Fe-contamination, especially in particulate form, may have deleterious effects on the strength of reaction-bonded silicon nitride. The role of Fe in the formation of RBSN deserves closer attention than it has hitherto received and, from the materials development standpoint, particularly, the manner in which the Fe is distributed within the Si powder compact.

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