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Kinetic interpretation of α- and β-Si_3N_4 formation from oxide-free high-purity silicon powder

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A kinetic analysis of the isothermal nitridation of high-purity oxide-free silicon powder is described. The kinetic analysis suggests that the α and β polymorphs of Si_3N_4 are formed by separate and parallel reaction paths. This analysis provides for the decoupling and quantitative kinetic interpretation of α- and β-Si_3N_4 formation reactions. Consistent with existing microstructural and thermodynamic evidence, the α-forming reaction is shown to obey a first-order rate law, whereas a phase-boundary controlled rate law describes the β-forming reaction. A kinetic model employing these rate laws is developed and is used to predict the α/β phase ratio as a function of isothermal reaction temperature and extent of reaction. The α/β phase ratios so obtained are shown to be in good agreement with experimental observations made under a variety of reaction conditions.

1. Introduction

The thermal nitridation of silicon is a practical and widely used commercial method for the production of silicon nitride powders [1]. A high α/β-Si_3N_4 phase ratio is advantageous in producing sintered bodies because the reconstructive α to β phase transition provides the driving force for densification [2] and produces a fibrous microstructure resulting in high mechanical strength [3]. At present, there is no general agreement regarding the global kinetics of the nitridation reaction and various global rate laws, including erratic [4], zero-order [5, 6], logarithmic [4], parabolic [7], and continuously diminishing kinetics [8], have been proposed. Even less definitive information is available regarding the relative formation kinetics of the α-Si_3N_4 and β-Si_3N_4 polymorphs. This is true, in part, because early kinetic studies of powder systems were obscured by trace impurities, both in the silicon powder and nitriding ambient, dramatically influencing both the nitridation rate and product phase composition [9]. This picture has been further complicated by the fact that some kinetic studies [7, 9] were performed under nonisothermal conditions and on dense powder compacts so that the effects of heat and mass transfer limitations could not be excluded.

Despite the complexity of the nitridation process in powder systems, a number of general observations are well established and have been thoroughly described in comprehensive reviews [10, 11]. Only a brief summary of the salient features of the nitridation process is repeated here. The α and β phase transition does not occur in the absence of a liquid phase at temperatures up to 1600° C [12], well above typical reaction temperatures [10]. The β to α phase transformation has never been observed [11]. Metallic impurities in the silicon powder, particularly iron, have a pronounced acceleratory effect on the reaction rate [13]. An acceleratory effect is also observed when hydrogen is added to the nitriding gas, and the combined use of iron and hydrogen may have a synergistic effect [14–16]. It has been shown [16] that the primary effect of these impurities is the removal of the native oxide layer on silicon, and it has been demonstrated [17, 18] that removal of the oxide layer prior to nitridation is essential if intrinsic reaction kinetics are to be studied. Iron and other metals forming low-melting silicon-rich eutectics enhance β-Si_3N_4 formation by providing a liquid precipitation medium for the reconstructive phase transition [11]. Depending upon conditions, addition of oxygen and hydrogen to the nitriding gas may enhance α-Si_3N_4 formation by encouraging active oxidation of silicon which is then nitrided in the gas-phase as $SiO_{(g)}$ [10]. Hydrogen is not expected to enhance α-Si_3N_4 formation under conditions where the native oxide layer has been removed by pretreatment [18]. The bulk of microstructural and other data suggest that α-Si_3N_4 is formed by a chemical vapour deposition (CVD) process while β-Si_3N_4 is formed by a gas–solid reaction [10, 11]. The chief influences of the various reaction variables have been recently summarized [11, 19] as shown in Table I.

From these observations it is apparent that decoupling the α-Si_3N_4 and β-Si_3N_4 formation kinetics requires: (i) removal of the native oxide layer on silicon prior to reaction; (ii) the use of high-purity silicon and nitriding gases; and (iii) preparation of powder samples to ensure that bulk transport effects are insignificant. Experimental data meeting these requirements have been provided by the careful investigations of Rahaman and Moulson [20] who measured

TABLE I Influence of reaction variables on silicon nitride products (reproduced in part from [11, 19])

Reaction variable	Influence on product
Time	Early reaction at low temperature produces high α/β phase ratio
Low temperature (< 1350° C)	High α/β phase ratio; fine structure
Medium temperature (1350 to 1410° C)	Texture becomes more coarse with increasing temperature; pore size increases
High temperature (> 1410° C)	β-Si_3N_4 encouraged; coarsens structure
High surface area	α/β phase ratio increases
High pressure	β-Si_3N_4 increases; texture becomes finer
High oxygen	α/β phase ratio increases
Hydrogen	α/β phase ratio increases; texture becomes finer
Iron	β-Si_3N_4 increases at high temperature
Flowing N_2 atmosphere	Encourages clean porosity
Heating rate	Various rates appear to alter α/β phase ratio; early reaction influences later reaction

the relative rates of α-Si_3N_4 and β-Si_3N_4 formation from deoxidized, high-purity silicon powders nitrided isothermally at 1623 K under a 95 vol % nitrogen/5 vol % hydrogen gas mixture. Unfortunately, no kinetic interpretation of the data was offered by the authors, other than to note that the nitridation behaviour was apparently comprised of three regimes corresponding to linear, continuously decreasing and zero reaction rates. We have recently re-examined the results of Rahaman and Moulson's study and recognized that a solid-state kinetic treatment of their data provides a quantitative interpretation of α- and β-Si_3N_4 formation reactions that is consistent with many previous experimental findings.

2. Kinetics analysis and results

Hancock and Sharp [21] have described a general method for the treatment of isothermal solid-state reaction kinetics. The treatment is based on the Johnson–Mehl–Avrami equation [22–24]

$$\phi = 1 - \exp(-\varrho t^m) \qquad (1)$$

or

$$-\ln \ln (1 - \phi) = \ln \varrho + m \ln t \qquad (2)$$

where ϕ is the fraction reacted in time t, ϱ is a constant that partially depends on the nucleation frequency and rate of grain growth, and m is a constant that varies with the system geometry. Hancock and Sharp have shown [21] that plots of $-\ln \ln (1 - \phi)$ against $\ln t$, with the restriction $\phi = 0.15$ to 0.5, yield approximately straight lines whose slopes, m, are indicative of the reaction mechanism. For $m = 0.54$ to 0.62, a diffusion-controlled mechanism is implied, whereas, for $m = 1.0$ to 1.24, a zero-order, first-order or phase-boundary controlled reaction mechanism is implied. A nucleation and growth mechanism is indicated when $m = 2.0$ to 3.0. The integrated forms of the various reaction rate expressions associated with these mechanisms are summarized in Table II. Differentiation between mechanisms within a given group is not possible from a knowledge of m alone; rather, precise experimental data to conversions approaching 100% are required [25]. It is therefore essential to test the individual rate expressions within a given group for values of ϕ approaching 1.0.

Using the data of Rahaman and Moulson [20] as described above, plots of $-\ln \ln (1 - \phi)$ against $\ln t$ for conversion of silicon to α-, β-, and $(\alpha + \beta)$-Si_3N_4 were made for $\phi = 0.15$ to 0.5 as shown in Fig. 1. The slope of the line for $(\alpha + \beta)$ formation lies substantially outside any of the ranges shown in Table II, indicating that the global kinetics are determined by more than one rate controlling process [21]. In fact, we

TABLE II Solid-state reaction rate equations

Function	Implied mechanism	Equation	m
$D_1(\phi)$	Diffusion controlled	$\phi^2 = kt$	0.62
$D_2(\phi)$	Diffusion controlled	$(1 - \phi) \ln (1 - \phi) + \phi = kt$	0.57
$D_3(\phi)$	Diffusion controlled	$[1 - (1 - \phi)^{1/3}]^2 = kt$	0.54
$D_4(\phi)$	Diffusion controlled	$1 - 2\phi/3 - (1 - \phi)^{2/3} = kt$	0.57
$F_1(\phi)$	First order	$-\ln (1 - \phi) = kt$	1.00
$R_2(\phi)$	Phase boundary	$1 - (1 - \phi)^{1/2} = kt$	1.11
$R_3(\phi)$	Phase boundary	$1 - (1 - \phi)^{1/3} = kt$	1.07
$Z_1(\phi)$	Zero order	$\phi = kt$	1.24
$A_2(\phi)$	Nucleation and growth	$[-\ln (1 - \phi)]^{1/2} = kt$	2.00
$A_3(\phi)$	Nucleation and growth	$[-\ln (1 - \phi)]^{1/3} = kt$	3.00

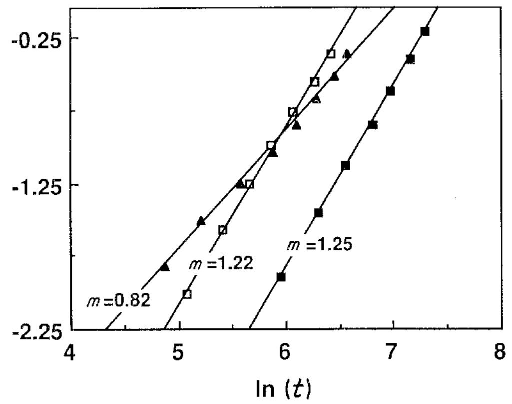

Figure 1 Plots of $-\ln \ln (1 - \phi)$ against $\ln t$ for conversion of deoxidized silicon to (□) α-, (■) β- and (▲) ($\alpha + \beta$)-Si_3N_4.

were unable to describe adequately the global kinetics (i.e. $\alpha + \beta$) using any of the ten standard reaction equations shown in Table II. On the other hand, if α and β formation kinetics are treated separately, the slopes of the lines ($m = 1.22$ and 1.25, respectively) suggest that these reactions obey zero-order, first-order or phase-boundary controlled rate expressions. A zero-order rate law can be immediately disregarded because neither α- nor β-Si_3N_4 formation was linear with time [20]. Consequently, only the individual rate expressions $F_1(\phi)$, $R_2(\phi)$, $R_3(\phi)$ were tested over the conversion range $\phi = 0.1$ to 0.975 and are compared for α and β formation in Figs 2 and 3. Fig. 2a shows that α-Si_3N_4 formation is best described by the first-order rate expression, $F_1(\phi)$, maintaining a linear least squares correlation coefficient > 0.999 over the entire conversion range examined. Figs 2b and c clearly show that expressions derived for a phase-boundary controlled mechanism are inappropriate in describing the α-forming reaction.

Conversely, Fig. 3a shows that the kinetics of β-Si_3N_4 formation do not obey a first-order rate law, while Figs 3b and c show they are well described by the phase-boundary controlled rate expressions. The best fit is obtained for the expression $R_3(\phi)$, as derived for the constant velocity movement of a reaction interface in a system with a spherical particle geometry. The linear least squares correlation coefficient for the fit of this rate expression was > 0.999 over the entire conversion range examined.

The observation that α- and β-Si_3N_4 formation kinetics are well described by different rate laws, while the global kinetics cannot be simply described, suggests that for the pure, oxide-free system, α- and β-Si_3N_4 are formed by separate and parallel reaction paths. This is corroborated by the finding that at 100% total conversion, no change in the α/β phase ratio was observed after 24 h at the reaction temperature [20], and indeed, no α to β phase transition is expected under conditions where a liquid phase is not present [12]. Parallel reaction paths were also proposed by Rahaman and Moulson [20] based on microstructural evidence and by Jennings [11] on thermodynamic grounds.

If parallel reaction pathways are assumed, then the differential forms of the individual rate expressions listed in Table II may be written to describe the formation rates of α- and β-Si_3N_4 as follows

$$(\mathrm{d}\phi/\mathrm{d}t)_\alpha = k_\alpha(1 - \phi_\alpha) \tag{3}$$

and

$$(\mathrm{d}\phi/\mathrm{d}t)_\beta = 3k_\beta(1 - \phi_\beta)^{2/3} \tag{4}$$

where ϕ_α and ϕ_β are the normalized conversions to α- and β-Si_3N_4, respectively. For example, ϕ_α represents the conversion of silicon to α-Si_3N_4 at time t divided by the total conversion of silicon to α-Si_3N_4. Consequently, ϕ_α and ϕ_β may each have values ranging from 0 to 1. The measured rate constants, k_α and k_β, were determined at 1623 K from the slopes of Figs 2a and 3c and have values of 1.00×10^{-3} and 1.68×10^{-4} sec^{-1}, respectively. Note that the rate constant, k_β, is the intrinsic phase-boundary controlled rate constant [26]

$$(k_\beta)^{\mathrm{i}} = k_\beta = (k/r_0) \tag{5}$$

where r_0 is the initial radius of the reacting particle. The instantaneous rate of β-Si_3N_4 formation is therefore as given by Equation 4.

On the other hand, the rate constant k_α must be considered an apparent first-order rate constant, because a first-order rate law has physical significance for geometry-independent reactions where the rate is proportional to the volume of material unreacted. Such a situation is typically only encountered in homogeneous liquid or vapour-phase batch reactions where, for an elementary reaction step, the reaction order is related to the molecularity of the reacting components. In materials systems, a first-order rate

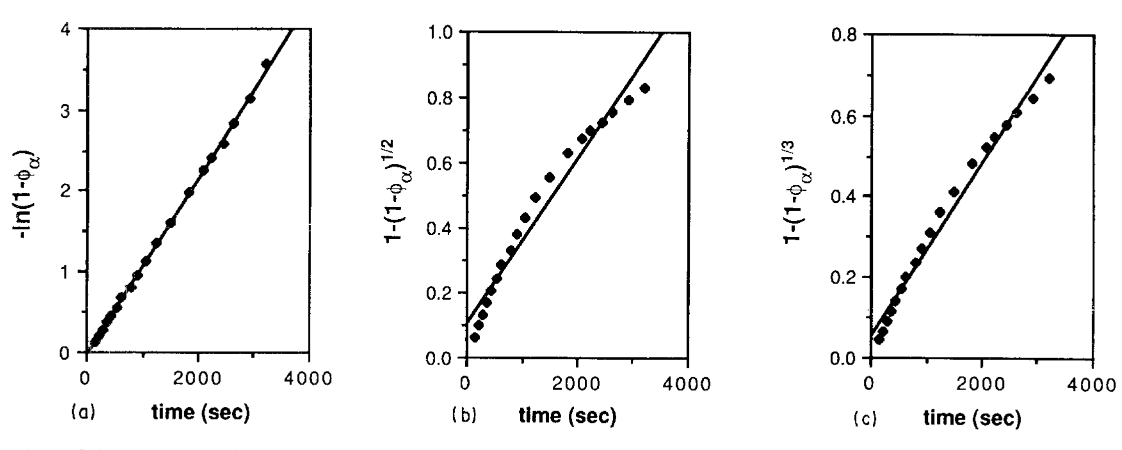

Figure 2 Plots of the rate expressions (a) $F_1(\phi)$, (b) $R_2(\phi)$, and (c) $R_3(\phi)$ against time for α-Si_3N_4 formation. The conversion variable, ϕ_α, refers to the normalized conversion of silicon to α-Si_3N_4.

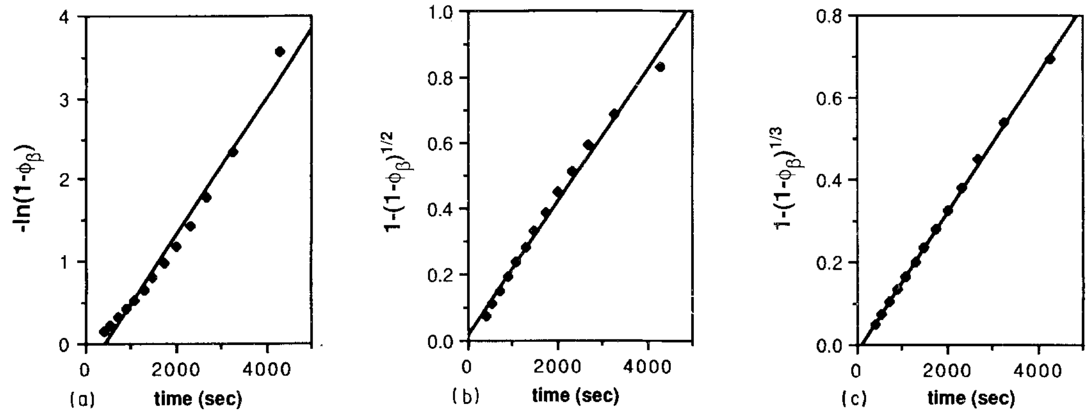

Figure 3 Plots of the rate expressions (a) $F_1(\phi)$, (b) $R_2(\phi)$, and (c) $R_3(\phi)$ against time for β-Si_3N_4 formation. The conversion variable, ϕ_β, refers to the normalized conversion of silicon to β-Si_3N_4.

law has meaning for a radioactive decay process, or for a nucleation-controlled process when there is an equal probability of nucleation at each active site [26], and so in each instance the system as a whole may be considered homogeneous. Silicon nitridation is, however, a heterogeneous gas–solid process and must necessarily involve an interfacial reaction [27]. With this in mind, if we consider the initial reaction rate, i.e. where ϕ approaches zero, it is evident that the silicon available at the reactive surface is small compared to the volume of unreacted silicon. It follows, therefore, that the intrinsic rate constant must be larger than the observed rate constant by a factor proportional to the surface area to volume ratio. Hence, if we assume spherical geometry for the silicon particles, we obtain at $\phi = 0$

$$(k_\alpha)^{\mathrm{i}} = (4\pi r_0^2 k)/(4/3\pi r_0^3) = 3k/r_0 = 3k_\alpha \quad (6)$$

where $(k_\alpha)^{\mathrm{i}}$ is the intrinsic first-order rate constant. We may now express the instantaneous rate of α-Si_3N_4 formation as

$$(\mathrm{d}\phi/\mathrm{d}t)_\alpha = (k_\alpha)^{\mathrm{i}}(1 - \phi_\alpha) = 3k_\alpha(1 - \phi_\alpha) \quad (7)$$

The global rate expression then becomes simply the sum of the two individual rate expressions

$$(\mathrm{d}\phi/\mathrm{d}t)_\mathrm{G} = 3[k_\alpha(1 - \phi_\alpha) + k_\beta(1 - \phi_\beta)^{2/3}] \quad (8)$$

For a parallel reaction sequence, the differential product selectivity ratio, $\mathrm{d}R/\mathrm{d}\phi$, for two reaction products i and j can be expressed [28] as

$$\frac{\mathrm{d}R}{\mathrm{d}\phi} = \frac{\text{instantaneous rate of formation of } i}{\text{instantaneous rate of formation of } j} \quad (9)$$

From Equation 9, the ratio of Equation 7 to Equation 4 then gives the differential α/β phase ratio

$$\frac{\mathrm{d}R}{\mathrm{d}\phi} = k_\alpha(1 - \phi_\alpha)/k_\beta(1 - \phi_\beta)^{2/3} \quad (10)$$

The differential α/β phase ratio in the limits of conversion can be explicitly determined from Equation 10 by noting that

$$\phi = \phi_\alpha = \phi_\beta \quad \text{at } \phi = 0, 1 \quad (11)$$

Equation 10 is then simply

$$\frac{\mathrm{d}R}{\mathrm{d}\phi} = (k_\alpha/k_\beta)(1 - \phi)^{1/3} \quad (12)$$

Equation 12 may be used to estimate the differential α/β phase ratio as a function of conversion by noting that $\phi \approx \phi_\alpha \approx \phi_\beta$ over all ϕ. This result is obtained by comparing the slopes of the kinetic fits in Figs 2a and c with those in Figs 3a and c respectively. In each case, the slopes are quite similar and therefore the condition $\phi \approx \phi_\alpha \approx \phi_\beta$ is approximately valid. Hence, provided the appropriate values of the individual intrinsic rate constants, $(k_\alpha)^{\mathrm{i}}$ and $(k_\beta)^{\mathrm{i}}$, have been independently determined from the best-fit rate laws, the α/β phase ratio at any conversion can be determined by allowing the normalized conversions ϕ_α and ϕ_β to be approximated by ϕ. We can now integrate Equation 12 over ϕ to calculate the integrated α/β phase ratio to be obtained at any fraction reacted

$$\int \mathrm{d}R = \frac{k_\alpha}{k_\beta}\int_{\phi_1}^{\phi_2}(1 - \phi)^{1/3}\mathrm{d}\phi \quad (13)$$

$$R = -\frac{3k_\alpha}{4k_\beta}(1 - \phi)^{4/3}\Big|_{\phi_1 = 0}^{\phi_2 = 1} \quad (14)$$

For the integration limits in Equation 14, the integrated α/β phase ratio, R, reflects the amount of α- and β-Si_3N_4 that would be measured in the sample at the completion of the reaction. Substituting the k_α and k_β values determined at 1623 K into Equation 14, an integrated α/β phase ratio of 4.46 is predicted. This corresponds to 82% conversion to α-Si_3N_4 and is in excellent agreement with the value of 81% measured by Rahaman and Moulson [20]. Consequently, the forms of the rate expressions in Equation 8 and the values of the associated rate constants are considered appropriate.

It is of considerable practical interest to predict the α/β silicon nitride ratio as a function of temperature and conversion so that an optimum nitriding schedule can be designed. This requires a knowledge of the temperature dependence of the rate constants, k_α and k_β, which cannot be determined from a single isothermal kinetic study. The temperature dependence of the rate constants can be approximated, however, if Arrhenius behaviour is assumed and a reasonable estimate for a (temperature independent) pre-exponential frequency factor is made. Applying the kinetic theory of gases [29], a pre-exponential factor of the order of $10^{13}\,\mathrm{sec}^{-1}$ is estimated at 1623 K. This value of the pre-exponential factor yields an activation energy of $119\,\mathrm{kcal\,mol}^{-1}$ for the α-Si_3N_4 forming reaction and

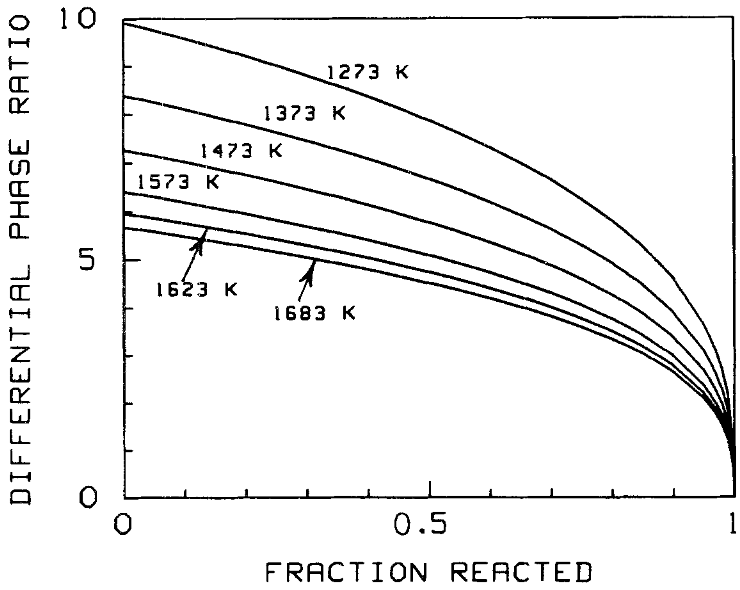

Figure 4 Calculated differential α/β phase ratio plotted against fraction reacted at various isothermal reaction temperatures for Si_3N_4 formation from deoxidized silicon powder.

125 kcal mol^{-1} for the β-Si_3N_4 forming reaction. These values fall within the range of 92 kcal mol^{-1} obtained by Hüttinger for the conversion of silicon to ($\alpha + \beta$)-Si_3N_4 from single crystal silicon [6] and 156 kcal mol^{-1} obtained for impure silicon powders [5].

The values of k_α and k_β estimated at various temperatures in the region where the reaction is likely to be isokinetic (i.e. below the melting point of silicon [5]) were used with Equation 12 to calculate the instantaneous α/β ratio as a function of fraction reacted, as shown in Fig. 4. It is seen that for typical nitriding temperatures (1273 to 1683 K), the differential α/β phase ratio at any conversion is constrained to lie within the range of approximately 0 to 10. At $\phi = 0$, the limiting α/β phase ratio, which represents the highest achievable α/β ratio at a given temperature, ranges from about 5.5 to 10. At $\phi = 1$, the limiting α/β phase ratio is 0 at all temperatures. At practical conversions [30] (i.e. ϕ slightly less than unity, ≈ 0.99) the limiting α/β phase ratio is ≈ 1 at all temperatures. The integrated α/β phase ratio determined from Equation 14 is plotted as a function of isothermal reaction temperature in Fig. 5. The integrated α/β phase ratio is predicted to occupy a somewhat narrower range than the differential phase ratio, resulting in a final product phase composition of $\alpha/\beta \approx 4$ to 7.5. Both Figs 4 and 5 predict high selectivity to α-Si_3N_4 at low temperatures and low conversions. Consequently, the α/β ratio is substantially fixed by the time-temperature profile maintained during the early stages of the reaction. It should be noted that in this model, the α/β phase ratio for any time-temperature schedule can be estimated by appropriate integration of Equation 12.

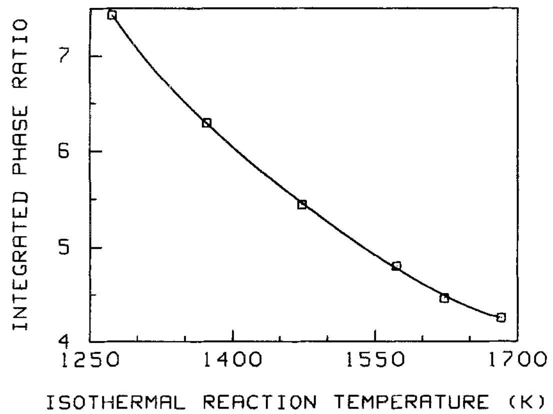

Figure 5 Calculated integrated α/β phase ratio plotted against isothermal reaction temperature for Si_3N_4 formation from deoxidized silicon powder.

3. Discussion

The above kinetic analysis agrees with earlier proposals based on thermodynamic [11] and microstructural arguments [20] that for oxide-free high-purity silicon powders, the α and β polymorphs are formed by essentially separate and parallel reaction paths. The kinetic model developed here indicates that the α-forming reaction is governed by a first-order rate law, whereas the β-forming reaction obeys a phase-boundary controlled rate law as derived for spherical particle geometry. While the mechanism underlying a solid-state reaction cannot be deduced on kinetic grounds alone, a first-order rate law is consistent with abundant microstructural evidence [3, 10, 11, 20] that α-Si_3N_4 formation results from a CVD process involving $Si_{(v)}$ and $N_{2(g)}$. In general, the molecularity implied by a first-order rate law only has meaning for an elementary step in homogeneous batch reaction systems, a situation that would appear illogical in the case of the heterogeneous silicon nitridation process. Alternatively, because the volatilization rate of silicon at typical reaction temperatures has been shown to exceed observed nitridation rates [10], it is possible to envisage that the first-order rate dependence of α-Si_3N_4 on silicon in fact arises from a homogeneous gas phase reaction of $Si_{(v)}$ and $N_{2(g)}$.

The mechanism implied by the phase-boundary controlled rate expression for β-Si_3N_4 is also consistent with the microstructural evidence [10, 20] that in the absence of a liquid phase, β-Si_3N_4 forms by the reaction of solid silicon with $N_{2(g)}$. Consequently, a rate law describing the movement of a reaction interface is expected. Given the assumptions of the kinetic model, no further speculations regarding possible mechanisms are offered.

Phenomenologically, however, the curves of Figs 4 and 5 predict the experimental findings of many investigators [10], as summarized in Table I. The model predicts high selectivity to α-Si_3N_4 at low temperatures and low conversions. The model further predicts that the time–temperature schedule maintained during the early stages of the reaction will have the greatest influence on the α/β phase ratio, also consistent with Table I. Furthermore, Moulson has stated in his comprehensive review [10] that any kinetic model must be consistent with the experimental finding that at temperatures in the range examined here, α/β phase ratios almost always lie between 1.5 and 9.0. Our model predicts the range to be 0 to 10 under limiting conditions, with practical limits of 1 to 10 more likely at reasonable conversions. (Quantitative conversion of silicon to Si_3N_4 is generally not achieved because some silicon is inevitably lost due to vapour transport [30].) The influences of pressure, iron, hydrogen, etc. involve reactions not related to the intrinsic nitridation process and their effects on the rate controlling process cannot in any simple way be related to isothermal nitridation kinetics. It is likely that these very effects hindered earlier attempts at a kinetic treatment of silicon nitridation [9].

It should be emphasized, therefore, that the predictions of α/β phase ratios presented here were based on measurements for high-purity deoxidized silicon powder under isothermal conditions. Because the total surface area of the powder available for reaction was not reported by Rahaman and Moulson, specific rate constants (i.e. per unit surface area) could not be determined. Large deviations from these conditions, particularly with respect to silicon purity, oxygen content and surface area, are likely to have a marked influence on the α/β phase ratio obtained. Nevertheless, the α/β phase ratios predicted by the model developed here are in excellent agreement with values obtained under a variety of other conditions [10, 11, 19]. Furthermore, the rate laws deduced for α- and β-Si_3N_4 formation are qualitatively consistent with the available microstructural evidence. It is expected that a kinetics model of this type can be developed to assist in the design of nitridation schedules whenever detailed data are available regarding the relative formation rates of the α- and β-Si_3N_4 phases.

4. Conclusion

The results of a solid-state kinetic analysis of isothermally nitrided high-purity, oxide-free silicon powder suggest the following points.

1. The α and β polymorphs of Si_3N_4 are formed by separate and parallel reaction paths.
2. α-Si_3N_4 formation obeys a first-order rate law.
3. β-Si_3N_4 formation obeys a phase-boundary controlled rate law.
4. Both rate laws are consistent with existing microstructural and thermodynamic evidence.
5. A kinetic model employing these rate laws and their associated rate constants predict integrated α/β phase ratios in agreement with experimental observations made under a variety of reaction conditions.

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