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The role of hydrogen in the nitridation of silicon powder compacts

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High-purity silicon powder compacts have been nitrided in nitrogen atmospheres containing varying partial pressures of hydrogen. The accelerated nitridation rates observed are interpreted in terms of the interaction of the hydrogen with the natural oxide film on the surface of the silicon particles. A model is presented for reactions taking place during the nitridation of these compacts in the presence of furnace atmospheres contaminated by low partial pressures of water vapour.

1. Introduction

Reaction-bonded silicon nitride is produced by nitriding compacts of silicon powder. Nitriding schedules are normally chosen so that the first stage of the reaction is carried out at temperatures below the melting point of silicon (~ 1410° C) in order to generate a structure-stabilizing skelton of silicon nitride. Completion of nitridation is then carried out at temperatures of up to ~ 1450° C in order to try to shorten the overall time required. Under normal conditions the lower-temperature nitridation of silicon powders tends to become unacceptably slow, and nitriding times of many days may be required for reasonably satisfactory degrees of nitridation [1].

A major research interest in this area in recent years has therefore been the search for ways of accelerating the lower-temperature nitridation of solid silicon, and of obtaining more rapid completion of the final 10% or so of the reaction. To this end, effort has been directed at understanding the function of commonly used accelerators such as metallic iron [2, 3] and certain metal fluorides [4]. The importance of the native silica film on the original silicon particle surfaces, and its nitridation-inhibiting action, is now well recognized [5–8]. It appears that many, if not all, of the reaction accelerators act on the silica film, causing its earlier disruption and loss, possibly by evaporation as silicon monoxide from an exposed $Si-SiO_2$ interface:

$$SiO_2(s) + Si(c) \rightarrow 2SiO(g)$$
$$\Delta G^{\ominus}_{1643} = 143\,\text{kJ mol}^{-1}. \qquad (1)$$

It is also recognized that any processing treatment likely to speed the elimination of silica films from the silicon–nitrogen interface leads to an acceleration of the early stage of nitridation. In this category can be placed, for example, pre-heating the compact in a vacuum or inert gas atmosphere at temperatures in the region of 1000° C [5], so that direct evaporation by dissociation becomes possible under the reduced oxygen partial pressure:

$$SiO_2(s) \rightarrow SiO(g) + \tfrac{1}{2}O_2(g)$$
$$\Delta G^{\ominus}_{1643} = 382\,\text{kJ mol}^{-1}. \qquad (2)$$

In this context attention has been paid particularly to the function of hydrogen, additions of which to the nitriding atmosphere have long been known to increase the overall rates of nitridation of silicon powder compacts [9, 10]. More recently further interest in the use of hydrogen has been stimulated by the realization that reaction-bonded silicon nitride formed under such conditions may also show improved mechanical properties compared with material prepared under nitrogen alone [11–14].

Investigations into the function of the hydrogen in this system confirm that one action is most probably the acceleration of the rate of removal of the protective native silica film on the silicon

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surfaces by the reaction [7, 8]:

$$SiO_2(s) + H_2(g) \rightarrow H_2O(g) + SiO(g)$$
$$\Delta G^{\ominus}_{1643} = 226\,\mathrm{kJ\,mol^{-1}}. \qquad (3)$$

The additional question remains, however, of whether there is a continuing subsequent function, such as the assistance of a nitridation reaction involving silicon monoxide vapour:

$$3SiO(g) + 2N_2(g) \rightarrow Si_3N_4(c) + \tfrac{3}{2}O_2(g). \qquad (4)$$

$\Delta G^{\ominus}$ for this reaction is large and positive ($545\,\mathrm{kJ\,mol^{-1}}$ at 1700 K) and as a minimum requirement an efficient sink for oxygen at low partial pressure ($\sim 10^{-16}$ atm) is required if the reaction is to be an effective source of silicon nitride. The presence of silicon monoxide within a nitriding silicon powder is virtually inevitable because there are three ready sources of the vapour: partial reduction of the native silica film, interaction of silicon with contaminated oxygen in the nitriding gas, and from water vapour contamination of the nitriding gas.

The possible contribution of Reaction 4 to the nitridation process has been critically examined by Moulson [1], who has focused attention on the important further requirement of an adequate flux of oxygen away from the growing nitride surface. It is suggested that hydrogen would be expected to sustain the reaction by forming water vapour at a theoretical equilibrium partial pressure many orders of magnitude higher than that of the oxygen. For example, with a hydrogen partial pressure of 10^{-2} atm the water vapour partial pressure corresponding to an oxygen partial pressure of 10^{-2} atm, the water vapour partial pressure corre- 1600 and 1700 K. A proportionately larger pressure gradient from the reaction zone would then allow sufficiently fast removal of oxygen to support the nitridation rates observed. In the absence of hydrogen it is supposed that Reaction 4 plays little part in the nitridation process, and that the nitridation of silicon vapour accounts for the formation of α-phase silicon nitride. (β-phase material is considered by Moulson to result from the nitridation of solid silicon, or of liquid phases.)

This argument differs substantially from that of Lindley and co-workers [13] who have assumed that, even in the absence of hydrogen, Reaction 4 is a major source of α-silicon nitride and that silicon surfaces or silicon vapour provide an adequate oxygen sink. The accelerating action of hydrogen is seen as that of raising the partial pressure of SiO within the nitriding compact through interaction with surface silica. The nitridation of silicon vapour, or of solid silicon surfaces, is then regarded as being responsible for the formation of β-silicon nitride. The higher partial pressures of SiO obtained in the presence of hydrogen are furthermore assumed to enhance formation of a skeletal network of silicon nitride, leading to improvements in strength of the final material.

It appears then that while the action of hydrogen in assisting commencement of nitridation is not disputed, the extent of its subsequent involvement with the several possible steps in the nitridation reaction, some aspects of which are considered to be of importance for the strength of the resulting material, is unclear. The purpose of the present study was therefore to examine the kinetics of nitridation of silicon powder compacts using a range of hydrogen partial pressures, in order to try to determine the extent of its involvement with the later stages of the nitridation process. In particular it was hoped that evidence might be obtained regarding the significance of Reaction 4 as a nitride-generating reaction, in view of the claims made [12, 13] for its importance for strength-developing processes. As far as possible, other likely variables in the nitridation reaction, such as temperature, gas flow-rate, powder size and purity, were maintained constant.

The experimental conditions chosen here represent therefore simplified conditions, in some respects far removed from the more complex and variable set of conditions found in commercial nitridations. The value to be gained from the use of such model systems has, however, been demonstrated [6]. It is clear that significant advances in the understanding of the nitridation process can only be made when close attention is paid to materials purity, and when other demonstrably important variables are isolated for individual examination.

2. Experimental details

Silicon powder was prepared from semiconductor-grade billet (> 99.999% purity), obtained from Monsanto Ltd, by crushing in a steel mill. The powder was then air classified to provide a fraction with particle sizes in the range 10–20 μm. This size range was selected because such silicon powders give conveniently fast nitridation rates, and approximate in particle size to commonly used commercial silicon powders [1]. Contaminating iron was removed as far as practicable by leaching with boiling 1 M hydrochloric acid, to give a final iron level as determined by atomic absorption spectrophotometry of 6.2×10^{-3} at %. Nitrogen gas and nitrogen–hydrogen gas mixtures (British Oxygen Company Ltd) were purified by passage through a bed of copper turnings heated at 200° C to remove oxygen, and then through dispersed phosphorus pentoxide to remove residual traces of water. The oxygen partial pressure and water-vapour partial pressures of the gas could be monitored continuously, both before and after their passage through the nitridation furnace, by the use of a calcia-stabilized zirconia oxygen meter and a commercial electrolytic hygrometer (Salford Electrical Instruments Ltd). With the purification system described, and with constant purging of the equipment when not in use, the water vapour level of gas emerging from the hot furnace could be reduced to the order of 10^{-4} atm. Levels less than this could not be maintained with any degree of consistency. The water vapour level of the gas leaving the purification system was undetectable ($< 10^{-6}$ atm) on the hygrometer used.

The vertical-tube furnace consisted of a sintered alumina tube (Morgan Refractories Ltd), heated by a winding of molybdenum wire. The heating element was protected by the same composition of gas mixture as was used in each nitridation experiment. This was because experience had shown that the alumina tubes tended to become permeable to hydrogen with use, so that the composition of the nitriding gas could be influenced by that of the element protection gas. Nitridations were carried out for varying lengths of time at 1643 K using ~ 500 mg compacts of silicon powder, at a constant gas flow-rate of $50 \text{ cm}^3 \text{ min}^{-1}$. Compacts were pressed isostatically without binder at 207 MPa to give a green density of $\sim 1600 \text{ kg m}^{-3}$.

Small compacts were used in order to give rapid thermal equilibration and to avoid the problem of internal temperature gradients due to the exothermic nature of the nitridation reaction [15]. Nitrogen flow-rate into compacts of this size would not be expected to be the rate-controlling factor [6]. The temperature of 1643 K, near the centre of commercial nitridation temperature ranges, allowed direct comparison to be made with kinetic data from previous investigations in these laboratories. Gas mixtures containing different proportions of nitrogen to hydrogen were prepared by blending the standard high-purity cylinder gases: nitrogen, nitrogen/5% hydrogen, nitrogen/20% hydrogen and pure hydrogen, using metered flow-rates. The silicon compact was held in a small, high-purity alumina crucible suspended by tungsten wire which could be rapidly (~ 1 minute) lowered into, and withdrawn from, the furnace hot-zone under the required gaseous atmosphere. The extent of nitridation was determined from weight-gain measurements made on the crucible and contents.

X-ray analyses of crushed nitrided compacts were made using a diffractometer and filtered CuKα radiation. Standard calibration curves based on the α_{201} and β_{101} peaks provided the proportions of the α- and β-phase in each product.

The calcia-stabilized zirconia oxygen meter was calibrated using standard CO/CO_2 gas mixtures giving oxygen partial pressures (at 1147 K) of 10^{-8} atm and 10^{-16} atm. The high-impedance millivoltmeter readings obtained agreed precisely with the theoretical values derived from the standard cell equation:

$$E = \frac{RT}{4F} \ln (p_1/p_2), \tag{5}$$

where E is the cell potential (V), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the cell temperature (K), p_1 and p_2 are the oxygen partial pressures on the two sides of the cell wall, and F is the Faraday constant ($96\,500 \text{ C mol}^{-1}$). The constant 4 appears because four units of charge are involved in forming oxide ions from one molecule of oxygen; p_2 was assumed to be 0.20 atm.

3. Results

3.1. Oxygen and water vapour partial pressures

Monitoring of these gas pressures was normally made on gas leaving the furnace hot-zone. After a short period of time, during which the furnace atmosphere stabilized, a fairly constant and reproducible water vapour pressure could be obtained. This was normally in the region of 10^{-3} atm. With prolonged purging with dry gas the level slowly fell with time to a value in the region of 10^{-4} atm. The actual level in the system during a nitridation run could in practice be maintained within these limits. It was clear that, in spite of prolonged purging with dry ($< 10^{-6}$ atm water vapour) gas, water vapour continued to be evolved from the metallic and oxide walls of the system which, with

TABLE I Typical water vapour and oxygen partial pressures at 1147 K

p_{H_2} (atm)	p_{H_2O} (atm)	p_{O_2} (calculated) (atm)	p_{O_2} (observed) (atm)
0	4.0×10^{-4}	8.6×10^{-9}	1.0×10^{-16}
0.005	4.4×10^{-4}	1.2×10^{-19}	3.2×10^{-19}
0.01	1.0×10^{-3}	1.6×10^{-19}	1.0×10^{-19}
0.05	1.7×10^{-3}	1.9×10^{-20}	1.0×10^{-20}
0.10	1.2×10^{-3}	2.3×10^{-21}	3.2×10^{-21}
0.20	6.0×10^{-4}	1.4×10^{-22}	3.2×10^{-22}

the materials of construction used, were not bakeable. These observations on the difficulties of obtaining a truly dry system are fully in accord with earlier comprehensive studies [17] of aspects of preparing and maintaining dry systems, and emphasize the need to take into account the presence of water vapour in a normal nitridation atmosphere.

On the basis of the hygrometer readings of the water vapour level, and the known hydrogen partial pressures, and assuming attainment of the equilibrium:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$$

$$\Delta G^{\ominus}_{1643} = -156\,\text{kJ}\,\text{mol}^{-1}, \qquad (6)$$

oxygen partial pressures were calculated for the temperature of the zirconia cell (1147 K). Examples of typical values are shown in Table I. Comparison of data for this temperature shows excellent agreement with the actual zirconia-cell readings, with the exception of the value for nitrogen alone. On the assumption that the water vapour content of the gas leaving the furnace approximates to that of the actual hot-zone and using Equilibrium 6, the oxygen partial pressure of the gas coming into contact with the silicon compact can be estimated. Examples of these values are shown in Table II. The calculated value of 1.6×10^{-4} atm hydrogen in "pure" nitrogen is derived from the measured oxygen and water vapour partial pressures. The origin of this hydrogen is uncertain but may be, for example, the result of small amounts of gas diffusing in from the protection gas around the furnace winding. In cases where silicon compacts were present in the hot-zone a ready source of low partial pressures of hydrogen would be the effectively quantitative reaction:

$$H_2O(g) + Si(c) \rightarrow SiO(g) + H_2(g)$$

$$\Delta G^{\ominus}_{1643} = -82\,\text{kJ}\,\text{mol}^{-1}. \qquad (7)$$

This is an important aspect and one which will be returned to in Section 4.

TABLE II Hydrogen and calculated oxygen partial pressures at a hot-zone temperature of 1643 K. Data derived from Table I

p_{H_2} (atm)	p_{O_2} (calculated) (atm)
1.6×10^{-4}*	7.3×10^{-10}
0.005	9.0×10^{-13}
0.01	1.2×10^{-12}
0.05	1.3×10^{-13}
0.10	1.7×10^{-14}
0.20	1.0×10^{-15}

*Calculated on the basis of oxygen partial pressure observed at 1147 K.

Later in the programme it became clear that a distinction needed to be made between the separate effects of varying hydrogen partial pressure and varying oxygen partial pressure. This was achieved by the deliberate enrichment of the gas stream with water vapour by bubbling it through a series of traps containing water at room temperature. In this way a water vapour level in the region of 0.03 atm was obtained without the need for the prevention of condensation in the gas lines. The corresponding calculated oxygen partial pressure at 1643 K and with 0.05 atm of hydrogen was 4.2×10^{-11} atm.

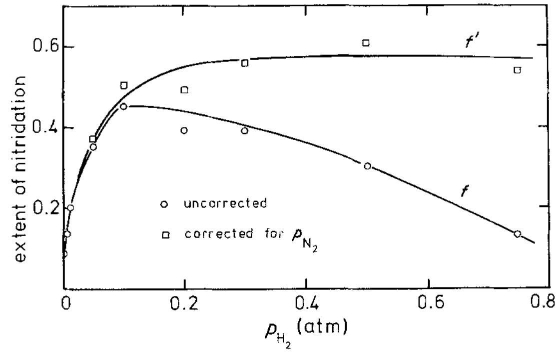

Figure 1 Observed extents of nitridation, *f*, and extents of nitridation corrected for p_{N_2}, f', as a function of hydrogen partial pressure for isothermal nitridation at 1643 K for 2 h.

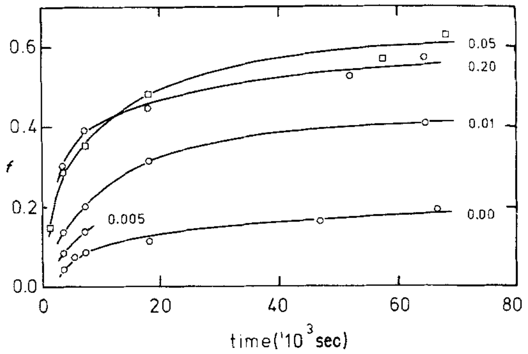

Figure 2 Observed extents of nitridation, f, as a function of time for isothermal nitridations under a range of hydrogen partial pressure (in atmospheres) at 1643 K.

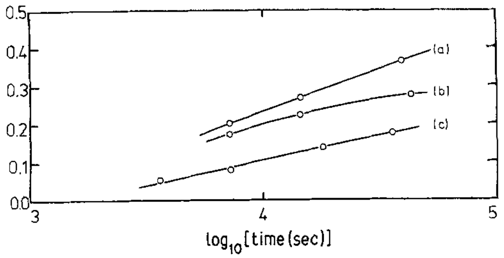

Figure 4 Extent of nitridation corrected for p_{N_2}, f', as a function of $\log_{10}t$ for isothermal nitridations with "dry" and "wet" gases at 1643 K. (a) Dry 0.05 atm H_2, (b) wet 0.05 atm H_2, (c) dry pure nitrogen.

3.2. Nitridation rates

Fig. 1 shows preliminary data for the observed extent of nitridation, f, after reaction of powder compacts in nitrogen at 1643 K for 2 h under a range of hydrogen partial pressures. The extent of nitridation is defined as the fraction by weight of the silicon converted to silicon nitride and therefore takes values from 0 to 1, the value of 1.0 corresponding to a weight gain of 66.49%. Fig. 1 also shows calculated values for the extent of nitridation of the silicon, f', made on the assumption that the reaction rate over this stage of the reaction, with a relatively small degree of conversion, is directly proportional to p_{N_2} [18]. Data points shown are therefore those of $f' = f_{obs}/p_{N_2}$.

A more detailed study of the effects of hydrogen partial pressure in the range 0 to 0.20 atm was then made over times up to ~ 18 h. Data for the observed extents of nitridation, f, of the silicon are shown plotted as a function of time, t (in seconds), in Fig. 2, and plotted corrected for nitrogen partial pressure as a function of $\log_{10}t$ in Fig. 3. Data points for experiments carried out with $p_{H_2} = 0.10$ are omitted for clarity; they overlap those of the 0.05 atm and 0.20 atm hydrogen points.

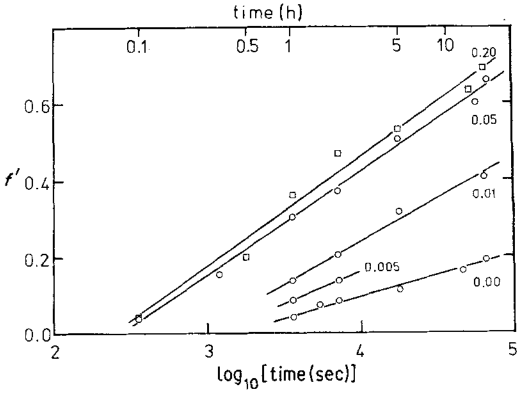

Figure 3 Extents of nitridation corrected for p_{N_2}, f', as a function of $\log_{10}t$ for isothermal nitridation under a range of hydrogen partial pressures (in atmospheres) at 1643 K.

The results of a separate series of experiments carried out on a new batch of silicon powder using "dry" and wet (~ 0.03 atm H_2O) N_2/5% H_2 gases are similarly shown in Fig. 4. Although this batch of powder was apparently closely similar to that of previously used powder the reaction rate in hydrogen is lower than expected. It would seem likely that this is the consequence of a difference in oxygen content between the two powders, but unfortunately facilities for a precise analysis of oxygen in silicon were not available.

The semi-logarithmic treatment of nitridation data has been used previously as a convenient means of deriving plots which are good approximations to straight lines [2]. It can be seen from Fig. 3 that the gradients of the plots increase slightly with hydrogen partial pressure up to a maximum in the region of $p_{H_2} = 0.05$ atm, above which level there is only a slight further increase. Extrapolated to $f' = 0$ the plots cut the $\log_{10}t$ axis at markedly decreasing times. This latter feature suggests the existence of a real but variable induction period in the nitridation process. Direct evidence for such an induction period has already been reported [6]. The precise length of the induction period cannot be derived from the kinetic data presented here, however, because of the absence of points for very short times (generally ~ 360 sec). Times shorter than ~ 360 sec could not usefully be used because of the likelihood of increasingly large errors due to the time taken for the alumina crucible and silicon powder compact to reach furnace temperature, and to cool again, on withdrawal from the hot-zone. Weight-gain measurements also tended to become imprecise at low extents of reaction. In the following discussion therefore the times of an "apparent induction period" are used, obtained by a simple straight-line extrapolation.

X-ray diffraction analyses made on crushed samples of all products showed that the proportion of α:β phase was, within experimental error, independent of time and hydrogen partial pressure, with a mean value of 83:17. For this reason separate plots of α-Si_3N_4 and β-Si_3N_4 phase yields are not shown.

4. Discussion

4.1. The effect of hydrogen additions on nitridation kinetics

The importance of hydrogen for the nitridation kinetics is shown unequivocally by a comparison of the observed instantaneous nitridation rates (df/dt) at a constant extent of reaction. Fig. 5 shows a plot of observed nitridation rates at $f = 0.15$, as a function of p_{H_2}, together with a similar plot corrected to take into account the decreasing nitrogen partial pressure with increasing hydrogen partial pressure. The justification for these corrections is the observation of Atkinson and Moulson [18] that in the early stages of nitridation:

$$\frac{df}{dt} = kp_{N_2}. \tag{8}$$

Nitridation rate data have been calculated using the least-squares fit equations for the curves plotted in Fig. 3, together with the curve, not shown there, for $p_{H_2} = 0.10$. A plot of nitridation rates (corrected for p_{N_2}) as a function of the calculated hot-zone values for $\log_{10}p_{O_2}$ is shown in Fig. 6. Figs 5 and 6 clearly indicate that a marked increase in the rate of the nitridation process occurs, either as the hydrogen partial pressure is increased through the range 0 to ~ 0.10 atm, or as the oxygen partial pressure of the gas surrounding the compact is reduced below ~ 10^{-12} atm. This apparent critical p_{O_2} value is of course higher by several orders of magnitude than the supposedly critical value derived from Equation 4 (~ 10^{-16} atm). On this criterion Reaction 4 could not occur; indeed the reverse of Rection 4, i.e. active oxidation of the silicon nitride, would be expected.

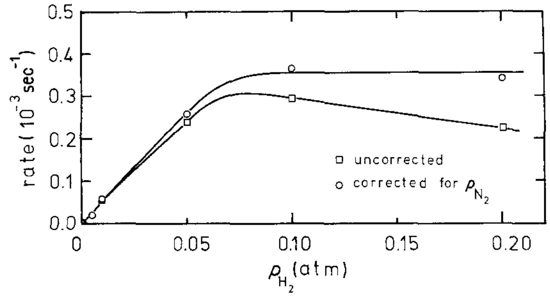

Figure 5 Nitridation rates for $f = 0.15$ and nitridation rates corrected for p_{N_2}, as a function of hydrogen partial pressure.

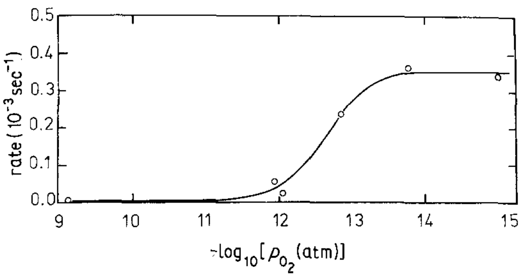

Figure 6 Nitridation rates corrected for p_{N_2} for $f' = 0.15$ as a function of $\log_{10}$ (oxygen partial pressure/atm).

A direct test of the effect of changing p_{O_2} at fixed p_{H_2} was attempted by increasing the water level from ~ 2 x 20^{-3} atm to ~ 3 x 10^{-2} atm. The results shown in Fig. 4 appear to confirm the observations of Mitomo [19, 20] and of Atkinson and Moulson [18] that the reaction rate (at constant hydrogen partial pressure) is essentially independent of oxygen partial pressure in the range 10^{-11} to 10^{-13} atm. The small relative reductions in rates observed at longer nitridation times using wet gas are readily explicable in terms of a linear rate-law loss of silicon monoxide by active oxidation of silicon or silicon nitride (Reaction 7). The large changes in reaction rate at constant extent of conversion shown by Fig. 5 appear therefore to be a direct function of hydrogen partial pressure.

It is clear therefore that the function of hydrogen in this system can be split into two elements. The first appears to be assistance with the removal of the protective silca film leading to a reduction in the length of an initial, very slow, reaction stage. In this respect maximum efficiency appears to be reached with 0.10 atm of hydrogen (Fig. 7). At this level the apparent induction period is of the order of 200 sec, or probably within experimental error of 0, in view of the time taken for a sample to equilibrate in the furnace hot-zone. Therefore, raising further the hydrogen

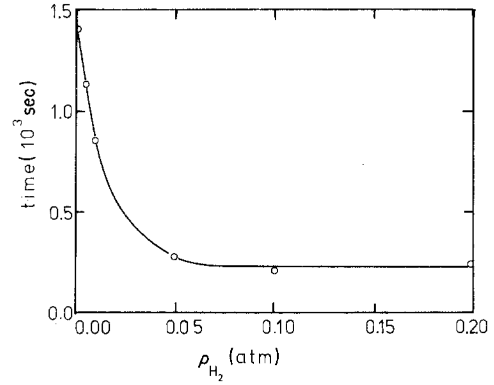

Figure 7 Apparent induction period plotted as a function of hydrogen partial pressure.

partial pressure is without benefit. Additionally, however, there is a second factor to be considered, in that the ensuing instantaneous nitridation rates, at constant extent of conversion, are also a direct function of hydrogen partial pressure. This aspect is examined in the following sections.

4.2. A model for a nitriding silicon powder compact

In order for the possible functions of hydrogen within a nitriding compact to be established, it is first necessary to construct a simplified model for the silicon powder/nitrogen system. It seems reasonable to regard the silicon powder compact in terms of two zones, illustrated schematically in Fig. 8. The outer zone, Zone I, is predominantly an oxidation zone within which the larger part of the oxygen or water vapour in the nitriding gas stream is converted to silicon monoxide or silica. The thickness of this zone will be a function of the oxygen and water vapour partial pressures but is likely to be in the region of a few hundred micrometres. Zone II is the main nitridation region within which the silicon monoxide level will be controlled by Reaction 1, with a limiting value for p_{SiO} at $\sim 10^{-3}$ atm. Here the hydrogen and nitrogen partial pressures will be those of the gas mixture supplied, the water vapour level is $\sim 10^{-7}$ atm (from Reaction 7, taking $p_{H_2} = 0.05$ atm), and the oxygen partial pressure a constant at $\sim 10^{-21}$ atom (from the dissociation

$$SiO(g) \rightarrow Si(c) + \tfrac{1}{2}O_2(g)$$

$$\Delta G^{\ominus}_{1643} = 238\,kJ\,mol^{-1}). \qquad (9)$$

The nitridation behaviour of silicon powder compacts will therefore be fundamentally different from that of silicon single crystal or polycrystalline slices, in that it would be expected to be relatively insensitive to the presence of oxygen or water vapour in the nitriding gas, even at fairly high partial pressures ($\sim$ 0.05 atm). This is fully in accord with present and earlier observations [12, 13, 19, 20].

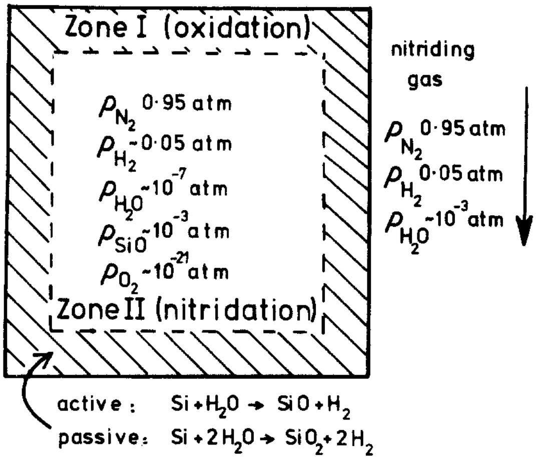

Figure 8 Two-zone model for the reactions of a silicon powder compact in normal nitrogen/hydrogen atmospheres.

Under normal nitridation conditions, with the virtually unavoidable presence of water vapour at $\sim 10^{-3}$ atm in the nitriding gas, the active oxidation (Reaction 7) of silicon in Zone I will supply a partial pressure of SiO at close to the maximum level permitted by Reaction 1 to Zone II. In the presence of higher external levels of water vapour, generated for example by deliberate enrichment experiments, an initially very high partial pressure of SiO in Zone I will be controlled by reversal of Reaction 1 to the Zone I–Zone II interface and the SiO partial pressure in Zone II would still be held to $\sim 10^{-3}$ atm.

A striking practical illustration of this "two-zone" concept is the recent report of the successful nitridation of silicon powder compacts "in air" where a sacrificial bed of silicon nitride powder is used as the Zone I material [21]. Earlier workers have also observed the formation of silica-rich skins on nitrided silicon powder compacts [22].

It immediately follows that the conditions with respect to oxygen and water vapour pressure under which nitridation occurs in Zone II are only indirectly related to the gas partial pressure near the Zone I–gas-stream interface, and monitored by the stabilized zirconia meter and hygrometer. The reasons for the acceleratory action of hydrogen additions need to be sought therefore in processes taking place in Zone II under effectively constant silicon monoxide and oxygen partial pressures.

It further follows that during nitridation under nitrogen alone and in the presence of water vapour (or hydrogen sulphide [23]) an approximately equal partial pressure of hydrogen will automatically be supplied to Zone II of the compact (Reaction 7). Water vapour might therefore be expected to show an apparent acceleratory action on the nitridation reaction, identical to that for hydrogen itself. Evidence for such an accelerating action has indeed be obtained [1, 18]. Kinetic data under such circumstances may not be easy to interpret, however, because of weight losses due to the simultaneous active oxidation reaction in Zone I. Data shown in Fig. 4 of the present study, for example, probably failed to reveal an acceleratory action of water in the presence of nitrogen/5% hydrogen presumably because of such a masking of the relatively small difference in reaction rate between 0.05 and ~ 0.08 atm of hydrogen (Fig. 5).

4.3. Reaction stages in the nitridation zone

The nitridation reaction in Zone II of a compact is usefully considered in terms of two stages. The first, slow stage occupies the period of time during which the protective silica film remains on the silicon surfaces, and the nitridation rate is probably close to zero. In the presence of the normal external atmosphere of $\sim 10^{-3}$ atm of water vapour passive oxidation will occur in Zone I by

$$\mathrm{Si}_{\mathrm{at\ Si/SiO_2\ interface}} + 2\mathrm{H_2O(g)} \rightarrow \mathrm{SiO_2(s)} + 2\mathrm{H_2(g)}$$

$$\Delta G^{\theta}_{1643} = -308\,\mathrm{kJ\,mol^{-1}}. \qquad (10)$$

reducing the water vapour level in Zone II to $\sim 10^{-7}$ atm, and proving a constant $p_{\mathrm{O_2}}$ at $\sim 10^{-21}$ atm, independent of $p_{\mathrm{H_2}}$. The corresponding equilibrium value of p_{SiO} is $\sim 10^{-3}$ atm, sufficiently large to allow rapid evaporation of Zone II silica in the presence of hydrogen through Reaction 3. Because this accelerated evaporation process requires hydrogen collisions with, or adsorption on, silica surfaces, the process is likely to be kinetically approximately first-order with respect to $p_{\mathrm{H_2}}$. The suggestion that this is the case is supported by Fig. 7. Whether the SiO formed diffuses out of the silicon compact, or whether it is converted internally into silicon oxynitride or an oxygen-containing α-silicon nitride would not be easy to establish, and is in any case not important from the point of the present discussion.

The second stage of the nitridation reaction can be considered to commence when loss of silica is complete in Zone II (and also probably in Zone I of the compact if the external water vapour partial pressure is sufficently low). Conditions in Zone II otherwise remain essentially unchanged, with p_{SiO} at $\sim 10^{-3}$ atm and $p_{\mathrm{O_2}} \sim 10^{-21}$ atm, with $p_{\mathrm{H_2}}$ determined either by the external water vapour level or by the partial pressure supplied with the nitrogen. In view of these considerations it seems unlikely that the action of hydrogen on the second-stage process can also be explained in the thermodynamic terms, and kinetic factors must again be examined. An immediate explanation is that hydrogen is able to accelerate formation of silicon nitride by assisting Reaction 4, as suggested by Moulson. The limiting rate effect seen at $p_{\mathrm{H_2}} \sim 0.10$ atm is, however, then difficult to understand. On the other hand, the close similarity between the observed effects of $p_{\mathrm{H_2}}$ at this stage, and those in the first stage make it tempting to believe that the two rate-controlling phenomena are directly connected.

A reasonable basis for this connection can be found in the observations of Raider [24] and Kooi [25] and their respective co-workers, on the formation of nitride films at a silicon–silica interface by the inwards diffusion of nitrogen through the thin silica film. The nitride so formed then acts as an effective barrier towards further nitridation. During the first stage of nitridation in Zone II of the compact, it may be postulated that a thin film of nitride develops under the surface silica film. After loss of the silica this nitride then remains during the second stage of the process to act as a barrier as effective as that of the original silica. Moreover, the lower the rate of removal of silica, the more effectively would the nitride layer be able to develop, and the slower would be the subsequent nitridation process because of a diminished surface area available for the supply of silicon vapour (Fig. 9). In terms of the pore-closure model discussed elsewhere [4], the area available for "pore" development would diminish with increased extent of nitride film development.

The observed relationship between length of induction period and rate of nitridation for $f' = 0.15$ is shown in Fig. 10. On this basis it would be expected that silicon powder compacts,

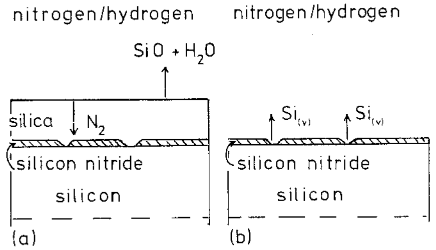

Figure 9 Schematic diagram of processes occuring at a silicon particle surface. (a) Initial formation of silica nitride film at the silicon–silica interface; (b) silicon vapour release subsequently controlled by this film.

from which silica had been removed under standard conditions before subsequent nitridation under a range of different hydrogen partial pressures, would show the same nitridation rate at a constant extent of conversion. Evidence that this is indeed the case has recently been obtained by Rahaman and Moulson [26], and the continuing apparent acceleratory action of hydrogen during the second stage of the nitridation reaction must be seen simply as a consequence of its interactions in the first stage of the process.

4.4. The silicon nitride-forming reaction

The experimental data discussed in the preceeding sections provide no evidence for the involvement of silicon monoxide in the silcon nitridation process. The evidence available suggests in fact that silicon monoxide is not involved. It appears likely that the rate of formation of silicon nitride during the major second stage is then largely controlled by the rate of release of silicon vapour from exposed silicon surfaces. Because of the strongly exothermic nature of the nitride formation reaction (− 877 kJ mol^{-1}) it is likely that, in the absence of liquid phases, the reaction only occurs at solid surfaces through reactions involving adsorbed or colliding species, and where the substrate can act as a heat sink. In this context it is also worth observing that the mean free path of a gas molecule at ~ 1650 K and 1 atm pressure is ~ 1 μm. Within the confines of a compact of particles of size ~ 5 μm, collisions of gas molecules with particle surfaces will predominate. Over larger distances diffusion would be of the Knudsen type, but within individual pores adsorption and desorption or surface diffusion would be expected to become the rate-controlling processes. Morgan [23] has drawn attention to an apparent "seeding" effect, through which α-phase or β-phase nitride crystals once nucleated continue to develop. It seems therefore that the "nitridation" step should be considered as a reaction between adsorbed Si or SiO and nitrogen at a silicon nitride surface. Oxygen formed through a hypothetical Reaction 4 could then be neutralized, still in an adsorbed state, by colliding Si atoms (partial pressure ~ 10^{-7} atm) or hydrogen molecules, or be desorbed to an adjacent silicon surface. Under these circumstances the distinction between adsorbed O$_2$ and adsorbed SiO must become blurred, and it is probably not helpful to think in terms of the nitridation of a recognizable SiO molecule.

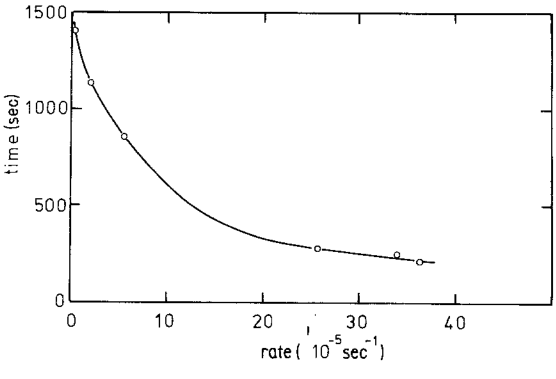

Figure 10 Apparent induction period plotted as a function of nitridation rate for $f' = 0.15$.

The observations of Lindley and co-workers [13] on the effects of hydrogen on the nature and properties of reaction-bonded silicon nitride require some comment in view of the arguments advanced above for the independence of p_{SiO} from $p_{\mathrm{H_2}}$ within the nitridation zone of a silicon powder compact. The action of hydrogen may be more simply regarded as that of modifying the growth morphology (perhaps most importantly in the earliest stages of the process as Lindley has recognized), through its action on the surface silica causing an early rapid release of silicon vapour and the development of a high density of growth nuclei.

Analysis of the data of Lindley and co-workers [13] after replotting using a log(time) axis indicates that in the flowing nitrogen system the apparent introduction period is prolonged, compared with that of a static system. The explanation for this may lie in the relative dryness of the flowing nitrogen stream, leading to correspondingly low hydrogen partial pressures within the silicon powder compact. Water vapour is likely to tend to accumulate in a static system, through continuous desorption from the furnace walls, and provide an acceleratory action through its conversion to hydrogen in the silicon powder compact. Deliberate enrichment of flowing nitrogen by water vapour is seen to compensate for the dry system [13], and to lead to material similar to that produced in static systems. It is clear, however, that more information on the precise water vapour (and hydrogen) levels as a function of time in practical static and flowing systems is required for a full analysis of this phenomenon.

5. Conclusions

This examination of the accelerating action of hydrogen in the silicon nitridation reaction indicates that its function is primarily to speed removal of the native silica film on the silicon powder particles. An induction period is thereby eliminated, and the continuing reaction rates are faster. It seems therefore that for a full understanding of the effect of hydrogen additions on the strength of reaction-bonded silicon nitride it is important that attention be focused on microstructural developments taking place within the first few minutes of the nitridation reaction. It is also clear that a short pre-treatment of a silicon powder compact under highly reducing conditions will be more effective in bringing about accelerated nitridation, than the simple addition of a small proportion (say 5%) of hydrogen to the nitriding gas. With very large additions of hydrogen reaction rates fall due to the nitrogen diluent effect.

Further conclusions with respect to the nature of the nitriding silicon compact system, and the importance of the presence of hydrogen and water in this system are as follows:

(a) The nitridation behaviour of pure silicon powder compacts can be modelled on the basis of a two-zone system, an outer sacrificial zone protecting the inner zone against large changes in the oxygen and water vapour contents of the nitriding gas stream, and in wet systems providing an important source of hydrogen.

(b) The function of this hydrogen or deliberately added hydrogen is primarily to accelerate the rate of reduction of the native silica film on the silicon particles in the inner (nitridation) zone of the compact. The speed with which this can be achieved determines to a considerable extent the surface area of accessible silicon and the eventual rate of development of nitride by reaction of silicon atoms transported via the vapour phase or surface diffusion, and adsorbed at nitride growth sites. In the presence of the silica film, slow silicon nitride growth is assumed to occur at the silica–silicon interface.

(c) Water vapour and other substances able to react with silicon to form hydrogen would be expected to show effects similar to those of hydrogen itself. Water vapour must therefore be regarded as an important variable in nitridation systems using nitrogen alone. Its effects will be screened to a very large extent when appreciable amounts of hydrogen are present in the nitriding gas.

(d) The gas flow-rate in nitriding systems may influence the course of the process by helping to determine the water vapour level in the vicinity of the powder compact, and consequently the hydrogen level within the compact. Even very low flow-rates may be expected to be significant in this respect, and this is also an effect which will be masked when nitridation is carried out in the presence of added hydrogen.

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