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Nitridation of Silicon Powder Studied by XRD, ^{29}Si MAS NMR and Surface Analysis Techniques

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Abstract

The nitridation of elemental silicon powder at 900–1475°C was studied by X-ray photoelectron spectroscopy (XPS), X-ray excited Auger electron spectroscopy (XAES), XRD, thermal analysis and ^{29}Si MAS NMR. An initial mass gain of about 12% at 1250–1300°C corresponds to the formation of a product layer about 0·2 μm thick (assuming spherical particles). XPS and XAES show that in this temperature range, the surface atomic ratio of N/Si increases and the ratio O/Si decreases as the surface layer is converted to Si_2N_2O. XRD shows that above 1300°C the Si is rapidly converted to a mixture of α- and β-Si_3N_4, the latter predominating >1400°C. In this temperature range there are only slight changes in the composition of the surface material, which at the higher temperatures regains a small amount of an oxidised surface layer. By contrast, in the interval 1400–1475°C, the ^{29}Si MAS NMR chemical shift of the elemental Si changes progressively from about −80 ppm to −70 ppm, in tandem with the growth of the Si_3N_4 resonance at about −48 ppm. Possible reasons for this previously unreported change in the Si chemical shift are discussed. © 1999 Elsevier Science Ltd. All rights reserved

Keywords: nitridation, X-ray methods, Si_3N_4, silicon.

1 Introduction

Silicon nitride, Si_3N_4, is widely used as an engineering ceramic, and its formation by direct nitration of elemental silicon has been extensively studied,[1,2] in view of the importance of the process for producing a dense product by reaction bonding.[3] Silicon nitridation by gas–solid reaction is a two-step process;[4] in the first stage, the surface SiO_2 layer devitrifies, allowing the exposed underlying Si to form $Si_2N_2O_4$. In the absence of a significant oxidised surface layer, or in the event of its removal as gaseous SiO[5] Si_3N_4 is formed by a nucleation and growth process[2] resulting in the formation of a product layer which inhibits further counter-diffusion of molecular N_2 and Si vapour. The favoured Si_3N_4 polymorph formed in this step is α rather than β, reflecting steric constraints between the N_2 molecule and solid silicon.[2] In the second stage, above the melting point of Si (1390°C), the reacting species is thought[2] to be atomic nitrogen which readily diffuses through the liquid silicon to form predominantly β-Si_3N_4. The rate of this energetically favoured process is diffusion-controlled.[2] Since the diffusion of nitrogen through the passivating nitride layer is comparatively slow,[2] the increased access of nitrogen to unreacted silicon in the second stage of the reaction may result from cracking of the surface layer when the underlying Si melts.

Recently we have developed a silicothermal process for synthesising a variety of sialons (β-sialon,[6] O′-sialon,[7] X-sialon[8] and α-sialon[9]). Nitridation of the elemental Si reactant is an important step in the silicothermal synthesis of all these materials. In the course of ^{29}Si MAS NMR studies of these synthesis mechanisms,[6–9] we have often observed a small but significant downfield shift of the ^{29}Si resonance of elemental Si from about −80 ppm to about −70 ppm. Since the latter value of chemical shift is well away from the known ^{29}Si shift for α-Si_3N_4 (−46·8 and −48·9 ppm[10]) and for β-Si_3N_4 (−48·7 ppm[10]), the reason for this previously unreported

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^{29}Si effect in elemental Si during nitridation is unclear. The present work was therefore undertaken to shed light on the circumstances under which this NMR shift occurs, and, since the phenomenon may involve the chemistry of the surface layers, to relate the shift to changes in the surface states of the sample grains, using surface analysis techniques previously applied by Okada *et al.* to silicon nitride powders.[11] These techniques (X-ray photoelectron spectroscopy and X-ray Auger electron spectroscopy) have been used to provide information about the surface layers of silicon nitride powders modified by grinding in various polar and non-polar solvents[12] and on the oxidised surface layers of silicon nitride and silicon oxynitride.[11] Since the present studies were carried out on the same commercial silicon powder used in silicothermal synthesis, which has an oxidised surface layer, these techniques, in combination with X-ray powder diffraction and solid-state ^{29}Si MAS NMR were expected to provide a new perspective on the nitridation of this starting material.

2 Experimental

The silicon powder (Permascand 4D, KemaNord Industrikemi, Sweden) was also used in previous sialon silicothermal synthesis studies[6–9] and had a particle size distribution measured by laser interferometer of 10% $<1{\cdot}0\,\mu$m, 50% $<4{\cdot}6\,\mu$m, 90% $<17{\cdot}7\,\mu$m. The manufacturer's analysis showed it

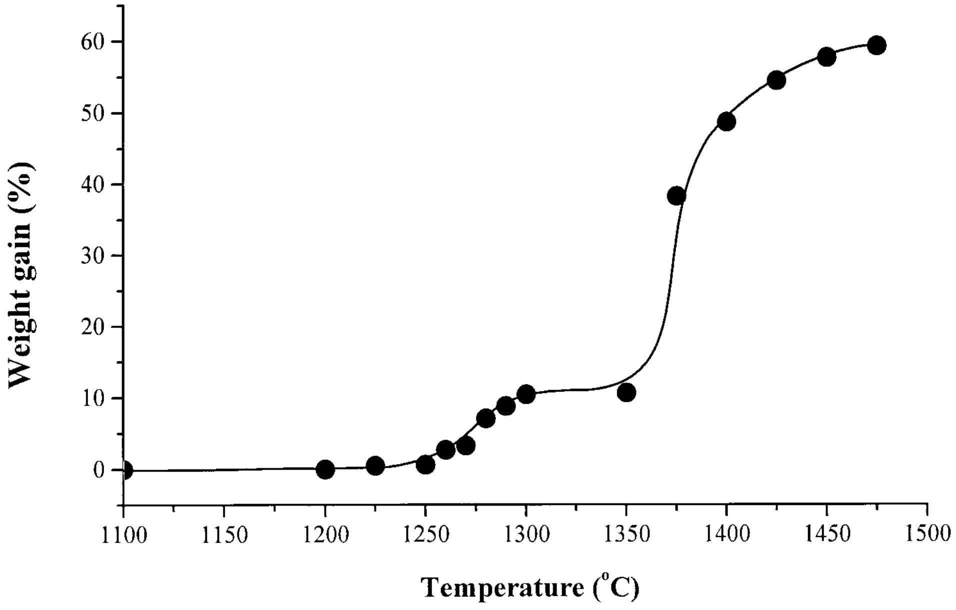

Fig. 1. Mass change in silicon powder heated in purified nitrogen gas.

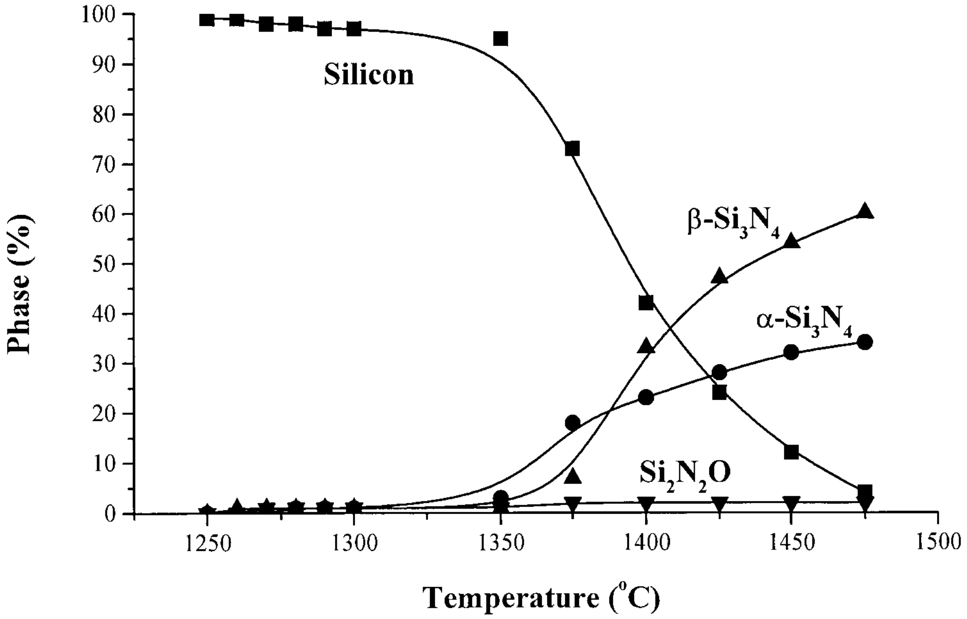

Fig. 2. XRD estimate of the bulk phases formed in silicon powder heated to the indicated temperatures in purified nitrogen gas.

to contain 0·2–1·0% O, 0·08% Fe, 0·08% Al, 0·01% Ca and 0·06% C. Powder aliquots (0·5 g) were nitrided in 10×15 mm alumina pots in flowing purified nitrogen (100 ml min^{-1}) in an electric tube furnace heated to 900–1475 °C at 5 °C min^{-1} then cooled at the same rate without a holding period at the top temperature. The samples were then examined by X-ray powder diffraction (Philips PW 1700 automated diffractometer with CoK_α radiation and graphite monochromator) and their ^{29}Si MAS NMR spectra obtained at 11·7T using a Varian Unity 500 spectrometer and 5 mm Doty MAS probe spun at 10 kHz. The spectra were acquired using a 10 μs $\pi/10$ pulse with a recycle delay of 100 s and were referenced to tetramethylsilane (TMS).

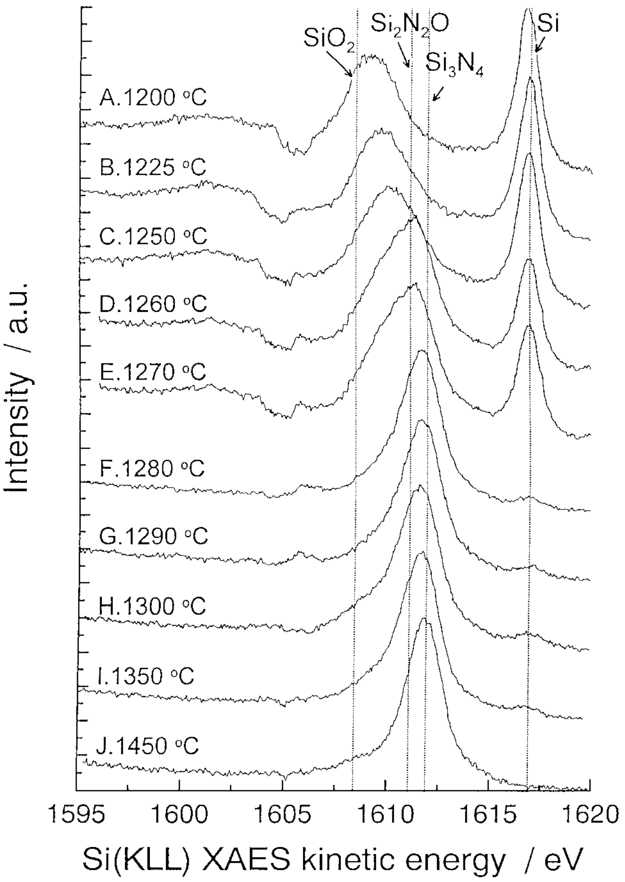

Fig. 3. Si KLL XAES spectra of silicon powder samples heated to the indicated temperatures in purified nitrogen gas.

The XPS and XAES spectra were obtained from the reacted powder, placed on Cu adhesive tape and mounted on a Mo sample holder. Charging of the poorly-conducting samples was neutralised by the use of a flood gun. The XPS equipment was a Model 5500MC (Perkin–Elmer Physical Electronics). Precise XPS measurements were made of the C1s, N1s and Si2p spectra using unmonochromated MgK$_\alpha$ radiation (15 kV, 300 W) and of the Si KLL XAES spectrum, using continuous X-ray radiation. The measurements were made at intervals of 0·05 eV with a pass energy of 11·75 eV and the spectra corrected to the C1s XPS peak at 284·6 eV arising from hydrocarbons deposited on the sample surface by evaporation of oil from the vacuum pump. Details of the curve fitting procedures and calculation of the Auger parameter (AP) are reported elsewhere.[11] The Si (KLL) XAES peak was used in this work to determine the surface chemical state of the samples since this Auger shift is usually larger than the Si2P photoelectron shift and can distinguish small changes more readily.

3 Results and Discussion

The percentage mass gain of the Si powder samples is shown in Fig. 1 as a function of the nitridation

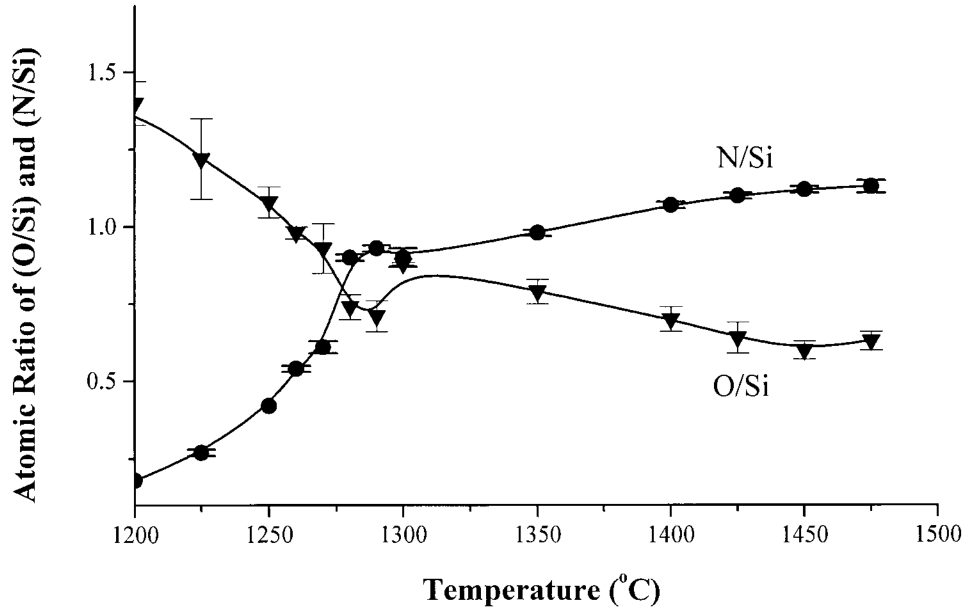

Fig. 4. Atomic ratios of the surface phase of silicon nitrided at various temperatures, deduced from the Auger parameter.

temperature. The initial small mass gain between 1250 and 1300 °C corresponds to 15% conversion to Si_3N4; if the particles are approximated as spherical with a mean radius of 2·3 μm, this represents a core of mean radius 2·1 μm surrounded by a spherical product layer of thickness 0·2 μm. After a further 50 °C temperature interval during which the mass remains unchanged, a rapid mass increase begins again, tailing off above 1400 °C as the theoretical value for full nitridation (66·7%) is approached. The general features of Fig. 1 were confirmed by thermogravimetric traces of the same silicon heated at 2 °C min^{-1} under flowing purified nitrogen gas.

The phase compositions at the various stages of the reaction, determined semi-quantitatively from the peak height ratios of the XRD powder diffraction traces, are shown in Fig. 2. The following reflections were used: Si, 111 at d=3.14 Å (PDF no. 27-1402), α-Si_3N_4, 210 at d=2·55 Å (PDF no. 9-250), β-Si_3N_4, 200 at d=3.29 Å (PDF no. 33-1160), Si_2N_2O, 020 at d=4·44 Å (PDF no. 33-1162). Figure 2 shows that the early stage (below 1350 °C) is accompanied by only a slight reduction in the Si XRD intensity; during the rapid mass gain >1350 °C the Si intensity decreases, with a corresponding increase in the intensities of both α and β-Si_3N_4. A trace of Si_2N_2O is also detected by XRD during the latter stages of the reaction.

A series of typical Si KLL XAES spectra of these samples in various stages of nitridation are shown in Fig. 3.

The un-nitrided material and that exposed to nitrogen below 1250 °C [Fig. 3(A) and (B)] shows two peaks, the broad feature at about 1609 eV corresponding to the surface SiO_2 layer, and the sharper peak at 1617 eV arising from the elemental Si. Heating to 1260 °C [Fig. 3(D)] produces a shift in the SiO_2 peak towards 1611 eV, the position of Si_2N_2O. As the heating temperature is increased >1270 °C, the oxynitride peak narrows and undergoes the further slight shift to become the Si_3N_4 peak at about 1612 eV. Surface nitration is therefore virtually completed in the present silicon in the narrow temperature interval between 1270 and 1280 °C; this corresponds to the small mass gain observed below 1300 °C. Further nitridation of the inner core up to 1475 °C produces no further change in the XAES spectrum of the surface Si_3N_4, but the slight shoulder on the low-energy side of this peak above 1300 °C [Fig. 3(H)] suggests the re-appearance of a small amount of oxidised surface material.

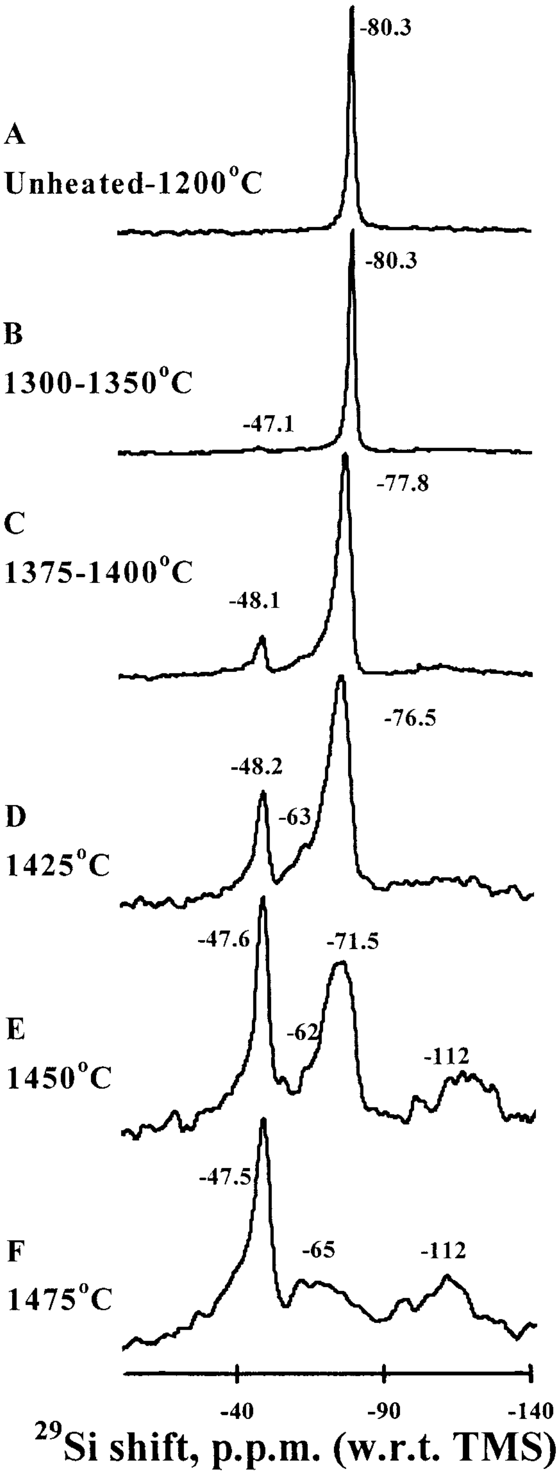

Fig. 5. Typical 11·7T ^{29}Si MAS NMR spectra of silicon powder heated to the indicated temperatures in purified nitrogen.

The XPS binding energy of these samples was also measured, allowing the Auger parameter (AP) to be calculated, since AP

$$AP = KE(KLL) + BE(K) \qquad (1)$$

where KE(KLL) is the kinetic energy of the Si(KLL) Auger electron transition and BE(K) is binding energy of the photoelectron, taken here as the Si2p photoelectron.

Following a previous treatment[11] the Auger parameters for these samples can be used to deduce the atomic ratios N/Si and O/Si for the present samples. These are plotted as a function of nitriding temperature in Fig. 4.

The change in atomic ratios with heating temperature indicates that in the first stage of the nitridation (about 1200 °C), nitrogen replaces the oxygen in the surface SiO_2 layer, which assumes the composition SiO_xN_y, where $x \gg y$. Between 1260 and 1280 °C, this phase and some of the underlying Si reacts with the nitrogen to form Si_2N_2O, which becomes the major surface phase. Above 1280 °C, Si_3N_4 formed by further nitridation of the oxynitride becomes the major phase, but is never free of a surface layer containing oxygen. At 1475 °C, the composition of this layer is approximately $Si_3N_{3\cdot4}O_{1\cdot9}$. The major nitridation mass gains above about 1400 °C are not accompanied by significant changes in the composition of the surface volume of the samples as detected by XPS and XAES (Figs 3 and 4) and therefore represent nitridation of the core material.

A selection of ^{29}Si MAS NMR spectra of samples at various stages of nitridation is shown in Fig. 5.

The ^{29}Si MAS NMR spectra show that during the early stages of nitridation (below 1200 °C) the bulk of the material is elemental Si, which has its characteristic chemical shift at −79 to −80 ppm [Fig. 5(A)]. In the present samples heated below 1300 °C, NMR does not detect the surface phases seen by XAES and XPS (above), but by 1300 °C, a small peak at −47·3 ppm characteristic of Si_3N_4 is detectable [Fig. 5(B)]. Between 1350 and 1400 °C, the Si_3N_4 resonance has grown at the expense of the elemental Si peak; the latter has also shifted to −77·8 ppm in the 1400 °C sample [Fig. 5(C)] and a small shoulder at about −61 ppm, characteristic of Si_2N_2O has also appeared. The Si_3N_4 resonance progressively grows on heating to higher temperatures, and the elemental Si peak continues to shift downfield, achieving a value of −71·5 ppm at 1450 °C [Fig. 5(E)] before merging into a broadened feature in the approximate position of Si_2N_2O at 1475 °C [Fig. 5(F)]. Changes in the distribution of ^{29}Si atoms over the various spectral regions, estimated by integration, are shown in Fig. 6 as a function of nitridation temperature. The changes in the chemical shift of the elemental Si resonance over the same high temperature range is shown in Fig. 7.

This small but progressive shift in the Si resonance to higher frequencies which occurs only in the final stages of nitridation does not appear to have been reported previously. There are two possible explanations for this effect:

i. As nitridation proceeds, the volume of the unreacted Si in the core of the nitride particle becomes increasingly small; calculations based on the weight gain of the powders in the temperature range 1400–1475 °C indicate that this core has a mean equivalent spherical diameter of 2·2–3·0 μm within this range. Since the paramagnetic contribution to the chemical shift is inversely proportional to the ‘average’ energy separation ΔE between the excited state energy levels and the ground state,[13] a decrease in the crystallite diameter leads to an increase in ΔE and a (downfield) shift to higher frequency, as observed here. The observed shift could thus be due to an increase in the bandgap of the Si core resulting from the reduction in its size.

ii. The pronounced tail at the higher frequency (lower field) side of the Si lineshapes in the temperature range of interest [Fig. 6(C)] is typical of a distribution of Knight shifts.[14] In Si doped with either phosphorus or arsenic,

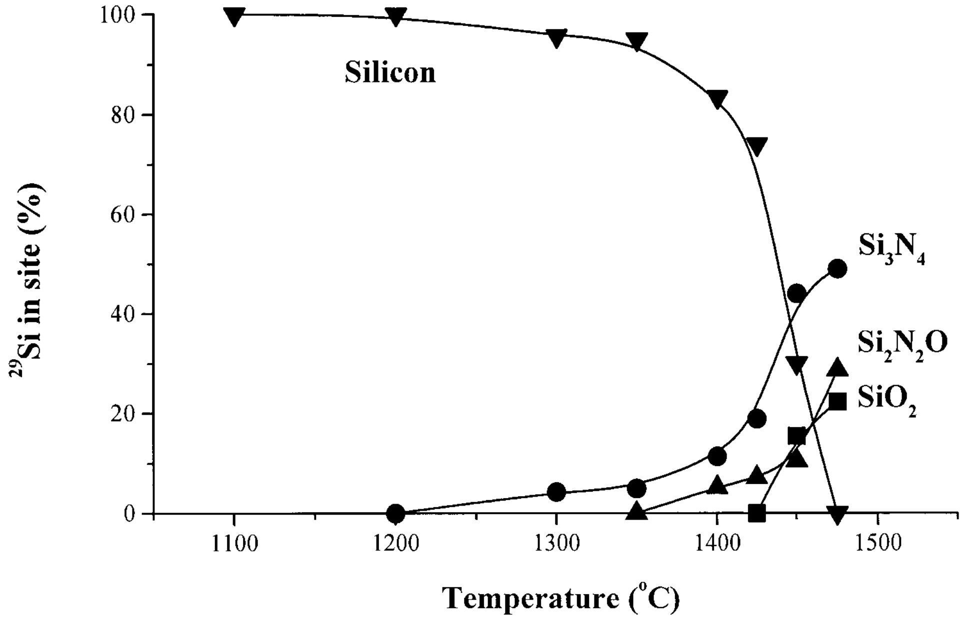

Fig. 6. Distribution of ^{29}Si in the various sites of silicon powder heated in purified nitrogen, as a function of temperature.

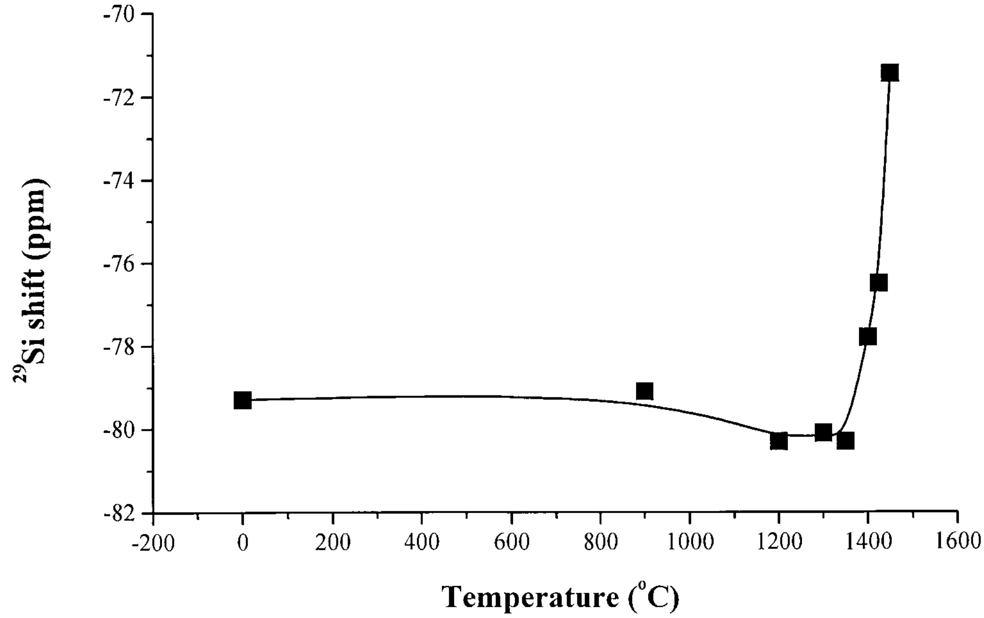

Fig. 7. ^{29}Si chemical shift of elemental silicon powder heated in purified nitrogen, as a function of temperature.

increasing the donor concentration leads to a linear increase in the Knight shift, resulting in a peak shift to higher frequency.[14] It is possible that the interaction of nitrogen with the elemental Si in the core particles increases in the later stages of the reaction due to the improved access of the nitriding atmosphere through cracks in the surface nitride coating. The increased donor concentration of nitrogen in the silicon could lead to an increase in the Knight shift, resulting in the observed movement of the Si resonance to higher frequencies.

At present it is not possible to say which of these two possible explanations is likely to predominate; both would lead to a shift in the observed direction, and these two effects may even be acting in tandem.

4 Conclusions

(a) The initial stage of nitridation of elemental Si powder is marked by the conversion of the oxidised surface SiO_2 layer and some of the underlying Si to Si_2N_2O. The thickness of this layer in the present experiments is estimated from the associated mass change to be about 0·2 μm.

(b) Little further reaction then occurs up to about 1350 °C, when rapid nitridation of the grain core material begins, forming a mixture of α- and β-Si_3N_4. The N/Si and O/Si ratio of the surface material is relatively unchanged during this phase of the reaction.

(c) In the later stages of nitridation, above 1350 °C, the ^{29}Si MAS NMR chemical shift of the elemental Si changes from about −80 ppm to about −70 ppm. This previously unreported change in the Si shift during nitridation may be due either to an increase in the bandgap of the Si as the core size of the reactant grains decreases in the last stages of the reaction, or to a change in the donor concentration of the Si due to interaction with nitrogen, resulting in an increase in the Knight shift. Both these mechanisms would explain the observed peak shift to higher frequencies; it is not possible to say which, if any, is the most likely to be operating.

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