controlled, as for example with PMMA in methanol. However, tests of this hypothesis do not appear to bear this out. Another example of unstable crack propagation in the absence of any environmental effects is with polystyrene [6]. Crack propagation is unstable when specimens are pre-cracked in a "normal" way. However, when a high frequency fatigue crack is put in the specimen as a starter crack, propagation is found to be continuous. The reason for this is thought to be the presence of branched crazes in the ordinary pre-cracked specimens and a sharp single craze at the tip of the fatigued crack. It may be that similar processes are taking place at the crack tip in epoxy resins although there is little evidence for crazing [4]. The phenomenon of crack propagation in epoxy resins is still not fully understood and we feel that there is still a great deal to be done before we have a complete answer to all the questions that can be raised.

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Received 15 March
and accepted 20 March 1978.

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The combined effects of Fe and H_2 on the kinetics of silicon nitridation

Mechanisms have recently been proposed to explain how Fe additions to silicon influence the nitriding reaction [1, 2]. It has been shown that Fe promotes the removal of the silica layer covering the silicon particles and, through liquid phase reactions, encourages the growth of β-Si_3N_4; it also promotes α-Si_3N_4 growth, and it was suggested that this occurs because the formation of Fe/Si liquid, at the reaction temperature, suppresses the development of the reaction-inhibiting coherent layers of nitride.

It is known that additions of H_2 to the nitriding atmosphere increase the nitriding rate [3] and influence growth morphology [4], and in this brief note we report some preliminary data relating to the combined effects of Fe and H_2 on the reaction.

Compacts were formed by isostatically pressing ($210\,MN\,m^{-2}$) specially prepared high purity silicon powder (particle size $<8\,\mu m$) [5]; where required, 0.5 wt% iron powder, having similar particle size, was well mixed with the silicon. The compacts were nitrided at 1360° C in a system described previously [5], the weight changes being monitored continuously to provide the kinetic data in Fig. 1.

The forms of the curves for pure and Fe-contaminated silicon, reacted in pure nitrogen (Curves A and B respectively) have been discussed previously [6]. The addition of 5 vol% H_2 to the nitriding gas (Curve C) leads to the expected marked increase on the overall reaction rate. The point we would like to stress here is the very fast kinetics for the iron-contaminated silicon, nitrided in N_2/H_2 atmospheres (Curve D).

A consideration of the rate of evaporation of Si at the reaction temperature and the observed rates of nitride formation, leads us to believe that the dominant nitriding reaction with pure N_2 is the vapour phase nitridation of silicon. This is contrary to a long-held view [7, 8] that the nitridation of silicon monoxide according to [1] is the major reaction.

$$3SiO(g) + 2N_2(g) = Si_3N_4(s) + \tfrac{3}{2}O_2(g) \quad (1)$$

Although the stated objection to Reaction 1 on thermodynamic grounds is invalid [9, 10], it can be excluded on kinetic grounds, since the rate of removal of oxygen from the Si_3N_4 formation site is many orders of magnitude too low to sustain the observed reaction rates.

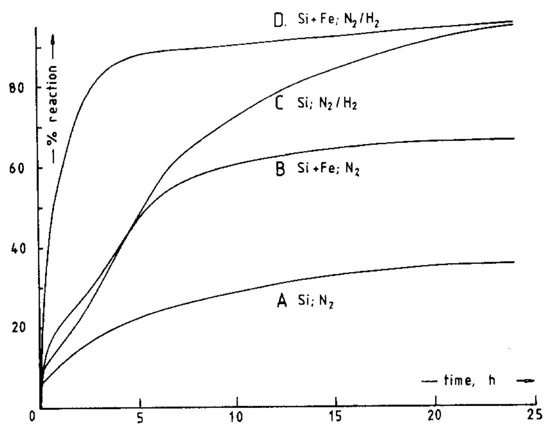

Figure 1 Per cent conversion of silicon to silicon nitride as a function of time for different nitriding conditions: Curve A – Pure silicon in nitrogen; Curve B – silicon–$\frac{1}{2}$ wt% Fe in nitrogen; Curve C – pure silicon in nitrogen–5 vol% hydrogen; Curve D – silicon–$\frac{1}{2}$ wt% Fe in nitrogen–5 vol% hydrogen.

However, it can be shown that, with additions of hydrogen in the range 1 to 10 vol%, together with H_2O in the p.p.m. range, the reaction rate for the nitridation of silicon monoxide can readily sustain the observed high nitridation rates, since oxygen can be removed quickly from the nitride sites as H_2O. This argument is developed in full in another publication [11].

It is known that the "sigmoidal" form of Curve B for the nitridation kinetics of Fe-contaminated silicon is related to the removal of the SiO_2 layer [6]. We would therefore interpret the similar characteristics of Curve C in a similar way, namely as indicating H_2-induced removal of the oxide layer, though not necessarily by the same mechanism. The overall faster reaction rate is then a consequence of Reaction 1.

Curve D, and Fig. 2 (which shows the early stage on an extended time scale) indicate that, together, Fe and H_2 have a cumulative effect upon the nitridation kinetics.

Is is suggested that a likely reason for this effect is a more extensive spreading of the ferrosilicon melt into the microstructure as a result of the hydrogen modifying wetting behaviour [12] and, in turn, reactive surface.

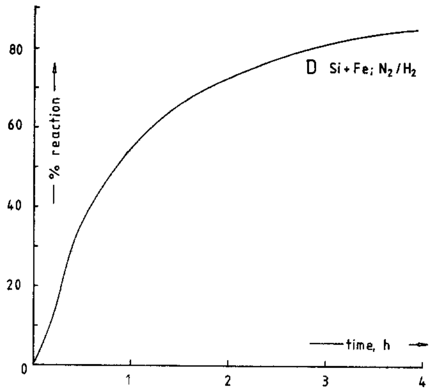

Figure 2 Per cent conversion of silicon to silicon nitride in early stages of reaction of Si–$\frac{1}{2}$ wt% Fe and N_2–5 vol% H_2 (Curve D).

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Received 31 January
and accepted 16 March 1978.

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