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The influence of iron and hydrogen in the nitridation of silicon

Interest in the presence of both iron [1, 2] and hydrogen [1, 3–5] in the silicon–nitrogen system has arisen in part because of their recognized capacity for accelerating the nitridation reaction. Dawson amd Moulson [6] have reported on the combined effect of iron and hydrogen, and comment on the apparently very fast kinetics observed as a result of a cumulative effect. We have recently examined a series of silicon powders of constant particle size distribution (10 to $20\,\mu$m; 350 m^2kg^{-1}) but of varying iron content, nitrided both under purified nitrogen and under nitrogen–5% hydrogen. These powders were obtained by crushing semiconductor-grade silicon billet in a cast-iron mill, followed by leaching in boiling 1M hydrochloric acid for different lengths of time to remove different proportions of the iron introduced during comminution. The minimum level of iron obtainable was 2.5×10^{-3} at.% and the maximum level used was 0.28 at.%. This iron was, therefore, "residual" iron, in contrast to the iron of Dawson and Moulson [6] which was added as ferric nitrate to acid leached silicon powder. Nitridations of small compacts (approximately 500 mg) were carried out in a molybdenum wound alumina tube furnace at 1630 K with a gas flow rate of 50 ml min^{-1}. The recorded water and oxygen partial pressures in the outlet gas from the reaction tube were 5×10^{-4} and 10^{-16} atm, respectively, for nitrogen, and 5×10^{-4} and 3×10^{-19} atm for nitrogen–5% hydrogen.

Nitridation data are presented in Figs. 1 and 3 using a linear time axis, and in Figs. 2 and 4 with a logarithmic time axis. The fraction of silicon reacted only is plotted; the α/β phase ratio in the product nitride remained constant, within experimental error, under all conditions at 85 : 15. The semi-logarithmic treatment provides a reasonable fit to most of the data points after an initial induction period. This indicates an experimental rate law over much of the time scale of the direct logarithmic type:

$$\alpha = k \log [at + 1]$$

where α is the fraction of reaction and k and a are constants, with departures also at very large values of t, as α approaches 1.0. A physical basis for this type of equation is provided by the mutual pore closure mechanism [7] in which reaction occurs only at a limited number of active sites, the number of which diminishes with time at a rate proportional to the reaction rate. However, while a pore closure mechanism might appear to provide a realistic model for the nitridation process in view of information available on the growth patterns of silicon nitride at clean silicon surfaces [8], and although earlier publications [9–11] suggests some generality for a logarithmic rate law, there are dangers in trying to deduce a reaction mechanism solely on the basis of an experimental rate equation. At this stage, therefore, we use this form of compressed time axis presentation as a matter of convenience, and without implying a particular nitridation mechanism. The practical merit of this form of presentation is that it allows quantitative comparisons to be made between different reaction curves over a considerable time scale, and especially after time intervals where the reaction rate is becoming very slow.

One feature of interest in these results, and shown clearly by Figs. 2 and 4, is that they confirm that an important acceleratory effect of hydrogen is due to a marked reduction in the length of an induction period (from the order of 10^3 to 10^2 sec), with subsequent fast initial

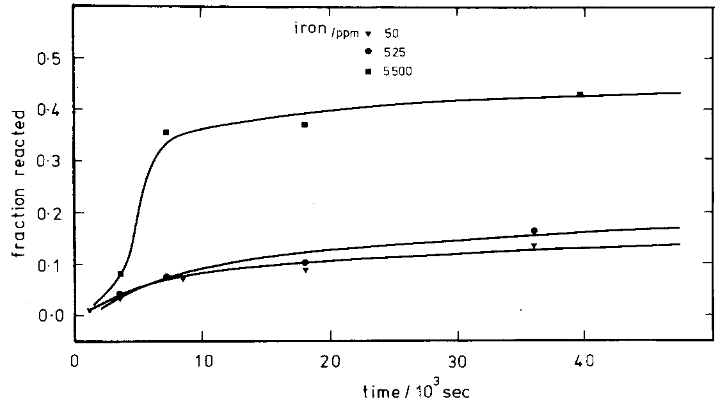
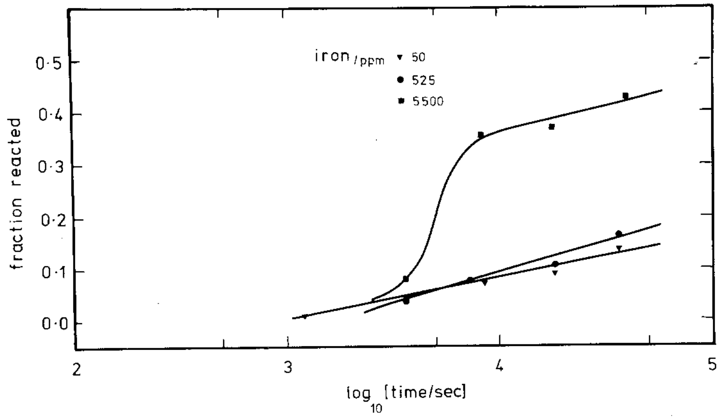


Figure 1 Extent of silicon nitridation at 1630 K under nitrogen as a function of time.

Figure 2 Extent of silicon nitridation at 1630 K under nitrogen as a function of $\log_{10}$ (time/seconds).



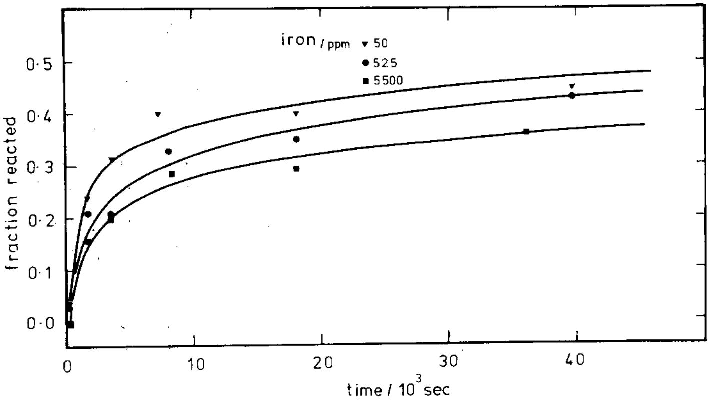


Figure 3 Extent of silicon nitridation at 1630 K under nitrogen–5% hydrogen, as a function of time.

reaction rates. In the absence of hydrogen initiation of reaction is inhibited, and the subsequent rate is sluggish unless a relatively large amount of iron is present, when a short-lived fast reaction occurs after about 4×10^3 sec. These effects are consistent with a model proposed by Boyer and Moulson [2], in which it is supposed that nitridation is normally inhibited by a thin silica film, which must be disrupted or removed before nitridation rates become significant. Hydrogen is clearly the more efficient agent in this respect. Values of the reaction rate at some specified extent of reaction provide a useful basis for quantitative comparisons, and data for $\alpha = 0.15$ are

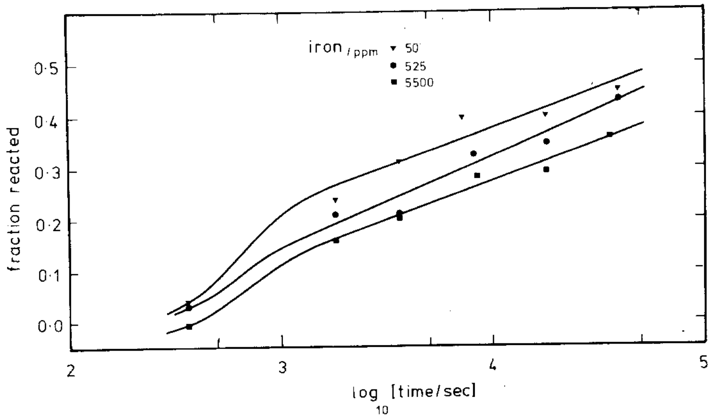


Figure 4 Extent of silicon nitridation at 1630 K under nitrogen–5% hydrogen as a function of $\log_{10}$ (time/seconds).

presented in Table I; the marked influences of iron and hydrogen at this stage of the reaction are also clear.

In the later stages of the nitridation under nitrogen the presence of iron is less noticeable, and the value of the logarithmic rate constant is within experimental error the same (as is also the case for nitridations under nitrogen–5% hydrogen). This is in agreement with the more detailed observations of Boyer *et al.* [12] concerning the transitory nature of the iron-accelerated stage of the nitridation reaction. It is also of interest that in the later stages the nitridation rate $d[\alpha]/dt$ at a specified time is approximately the same for the heavily contaminated silicon sample as for the powders with low iron contents, even though the extent of reaction is very different. The silicon nitride fomed rapidly as a result of the presence of iron does not appear to interfere with the succeeding reaction, a feature suggesting the absence of rate control by time-dependent diffusional processes.

The reversed effect of varying levels of iron contamination on nitridation in the presence of hydrogen is unexpected. It suggests that the form of the iron is important, and that the residual iron, which may be present as discrete particles, is not able to have the same effect as iron added to the silicon powder, and perhaps dispersed more homogeneously. This effect has to be investigated more closely. If the function of the iron were simply to accelerate loss of silica, then since hydrogen is the more efficient, under hydrogen the presence of iron would be undetectable. Slight sample weight losses observed after very short reaction times with nitrogen–5% hydrogen in the presence of a large amount of iron indicated a more marked loss of SiO from the compact. This in itself would be insufficient, however, to account for the observed difference in reaction extent at constant time.

TABLE I Nitridation rates at constant extent of reaction ($\alpha = 0.15$)

Iron (at.%)	$\frac{d[\alpha]}{dt}$ $(10^{-6}\,\text{sec})$	
	N_2	N_2–5%H_2
0.0025	1.1	580
0.026	3.5	230
0.28	300	120

Evidence for a continuing rate-controlling action of hydrogen in the nitridation process is provided by the larger values of the experimental logarithmic rate constant for nitrogen–5% hydrogen (mean value 0.16) compared with those for nitrogen alone (mean 0.10). This is signficant because it shows that hydrogen is involved in the normal rate-controlling process, and that its function is not solely that of aiding removal of the reaction inhibiting silica film from the silicon.

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