Nitridation of high-purity silicon

In an earlier paper [1] micrographs of partially nitrided silicon powder particles were shown and a nitridation mechanism proposed to explain them. An extensive study of this reaction was subsequently undertaken to understand the mechanism in greater detail. Particular attention has been given to attaining high purity silicon powder (< 10 ppm metallic impurities) and nitriding atmospheres (3 ppm water vapour and < 1 ppm oxygen). The kinetics of nitridation and morphology of the growing nitride have been studied as functions of temperature (1200 to 1400° C) and nitrogen pressure (0.03 to 1 bar).

It is generally acknowledged that the purer the silicon, the more difficult it is to nitride [2]. The present experiments, however, demonstrate that nitride layers of thickness ~ 20 μm can readily be formed on pure silicon particles when using a low nitrogen pressure. This observation has considerable significance for the production of reaction-bonded silicon nitride from high purity silicon. The experiments also show how the reaction kinetics are related to the microstructure of the nitride.

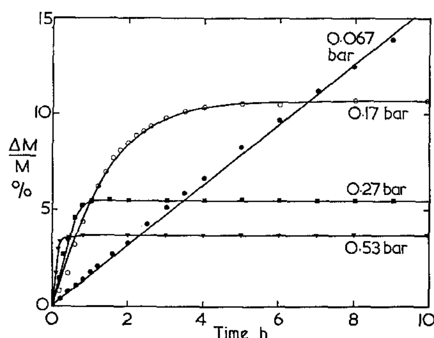

Figure 1 Nitridation kinetics of compacts of 75 to 100 μm silicon particles at 1370° C and the indicated pressures.

High-purity powder was prepared from ingots of undoped semiconductor grade silicon (Monsanto, Ghent, Belgium) by first crushing in a steel-lined "Shatterbox" (Glen Creston Ltd, Stanmore). The powder was sieved to provide a size fraction in the range 75 to 100 μm. This fraction was washed in 1 N HCl for 3 days and finally with distilled water to remove metal contamination. After this treatment none of the significant impurities (e.g. Fe) could be detected spectrographically. From oxygen analysis (by neutron activation) it was inferred that the silicon surface was covered with an oxide film of thickness ~ 3 nm. The powder was pressed isostatically into 0.5 to 1 g cylindrical compacts. Each was then nitrided in a thermogravimetric apparatus together with a lapped and electropolished {III} silicon crystal slice (Monsanto) of comparable purity. A zirconium getter adjacent to the samples maintained the oxygen content of the nitrogen below 1 ppm. The samples were first heated *in vacuo* (~ 10^{-7} bar) at 1370° C for 15 min to remove the oxide film (the loss being monitored by the balance). Nitrogen was then admitted to a desired pressure which was stabilized by means of a Cartesian monostat.

In Fig. 1, the mass of nitrogen reacting with unit mass of silicon is plotted against time for

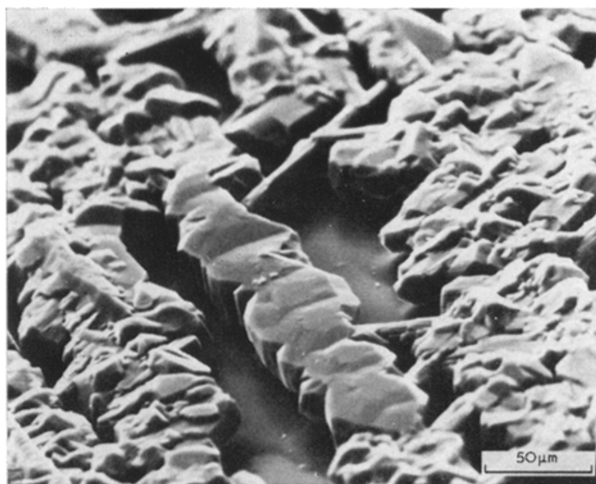

Figure 2 Scanning electron micrograph of the surface of a {III} crystal after nitridation for 18 h at 1370° C and 0.067 bar.

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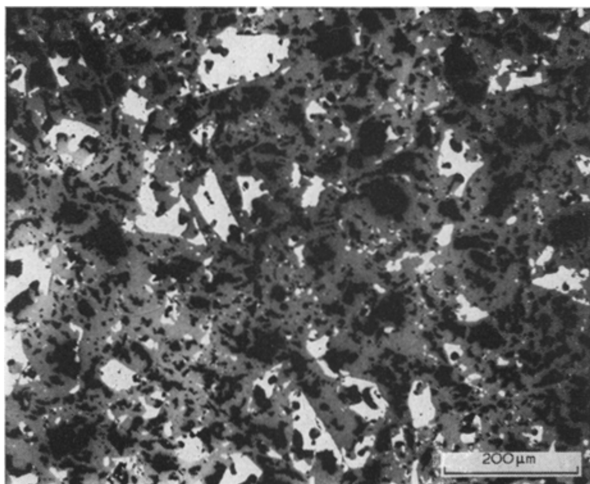

Figure 3 Optical micrograph of a polished section of a compact nitrided for 60 h at 1360°C and 0.067 bar. (White, silicon; grey, nitride; black, porosity).

different nitrogen pressures. The curves show three distinct regions. Initially, the kinetics are linear, then the rate decreases until, finally, nitridation effectively ceases. Although the linear rate increases with increasing nitrogen pressure, the most interesting feature is that more nitride is eventually produced at lower nitrogen pressures.

Fig. 2 is a scanning electron micrograph of the surface of a silicon slice after reaction at 0.067 bar in the regime of linear kinetics. It shows the surface of the silicon to be only partially covered with nitride. It is thought that the gradual departure from linear kinetics is related to the progressive occlusion of the silicon surface until finally, with complete coverage, the nitridation rate becomes negligible. That this coverage is attained more rapidly at higher nitrogen pressures is probably related to the associated increases in the nitride nucleation rate and density.

The microstructure of a compact nitrided to this final stage is shown in Fig. 3. The nitride formed amounts to 75% conversion of the original 75 to 100 μm particles. From this it is estimated that pure particles of up to 30 μm diameter may be nitrided completely using low nitrogen pressures. A characteristic feature of this reaction is the occurrence of pores within the silicon particles (Fig. 3). It was evident from examination of the single crystal and the compacts that the pores were formed by the evaporation or surface diffusion of silicon from uncovered areas of the surface. Furthermore, the transport of both silicon and nitrogen was via gaps in the nitride deposit and not by solid-state diffusion as previously thought likely [1].

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Synthesis of the α form of silicon nitride from silica

The synthesis of silicon nitride powders by reaction between silica, carbon and nitrogen has been well known since a German patent was granted in 1896 to Mehner [1]. However, the reaction seems to be more complicated than the reaction between silicon and nitrogen elements, which is generally used for the production of commercial silicon nitride, because of the simultaneous formation of silicon oxynitride (Si_2ON_2), silicon carbide (SiC) and the existence of unreacted silica. Because of the wide availability of silica and carbon of very high purity and fine particle size from commercial sources,

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