The effects of hydrogen on the nitridation of silicon

Attention is drawn in a recent short communication [1] to the marked increase in silicon nitridation rate obtained by the addition of a small percentage of hydrogen to the nitriding gas. While the general action of hydrogen has been known for some time [2, 3], until recently little effort seems to have been made to identify precisely the function of the hydrogen and to study the kinetics of the processes involved. The sigmoidal characteristics of the overall reaction curve for the nitridation of iron-free silicon in nitrogen/5% hydrogen [1] were taken to indicate that hydrogen assists the removal of a reaction-inhibiting oxide film on the silicon surface, an effect similar to that obtainable from a pre-treatment under a low partial pressure of oxygen in argon at 1370° C [4].

Direct evidence for the action of hydrogen in assisting the initiation of the nitridation process has been provided by the use of nitrogen/5% hydrogen in a low temperature pre-nitridation stage. Small compacts of two commercial silicon powders, the characteristics of which are shown in Table I, were heated for 2 h at 1000° C in a slow stream of gas. The compacts were then temporarily moved into the cool zone of the furnace while the temperature was raised to 1365° C and the nitrogen/hydrogen mixture replaced by purified nitrogen. The subsequent nitridation behaviour of the silicon is shown in Table II. Yields of the α and β-phases of silicon nitride are expressed in terms of weight of product per 100 units of weight of silicon, and the reference data are for nitridations carried out without the hydrogen pre-treatment, but under otherwise identical conditions.

TABLE I Silicon powder characteristics

Silicon powder	Mean particle size (μm)	Major impurity levels (wt %)				
		Al	Fe	Ca	Cu	O
B	23	0.67	0.76	0.06	0	1.60
D	20	0.45	0.43	0.03	0.45	0.30

TABLE II Nitridation behaviour of silicon powder compacts at 1365° C

Silicon powder	Nitridation time (h)	Product yields			
		Without pre-treatment		Following pre-treatment	
		α	β	α	β
B	2	13	16	28	33
	4	18	25	24	50
D	2	15	18	34	60
	4	23	30	23	67

While this small number of results show some scatter, presumably due to the difficulties of obtaining controlled reductions without risk of subsequent slight reoxidation, the general conclusion is clear. It is of further interest that the effect of hydrogen on the β-phase forming process tends to be more marked than that on α-phase reaction. This is interpreted as indicating a more active role subsequently for the metallic impurities (notably iron) in these powders once the oxide film has been removed, possibly through a more widespread wetting of clean silicon surfaces. Under normal nitridation conditions this redistribution of metallic impurities may still occur, but only after relatively long periods of time [5]. The association between β-phase formation and the presence of iron in the silicon powder during nitridation in nitrogen is well established [5–7].

From the practical standpoint of achieving faster formation rates of reaction-bonded silicon nitride at lower temperatures, any procedure which has the effect of generating a sufficiently low oxygen potential within the silicon powder compact will serve to remove the protective oxide films from the silicon particles. The critical oxygen pressures in the case of pure silicon can be estimated, following the approach of Wagner [8], to be of the order of 1.3×10^{-13} atm at 1000° C and 3×10^{-8} atm at 1410° C. Pressures as low as these would be difficult to achieve under nitrogen or vacuum conditions. However, metallic impurities able to devitrify the silica film so as to expose the underlying silicon [7, 9] may raise these critical pressures to 3×10^{-6} and 1.5×10^{-2} atm, respectively, and these are readily obtainable with a pure inert gas such as argon, and with nitrogen. Argon [4] appears, in practice, to be more effective than nitrogen in securing the evaporation of silica from silicon contaminated by iron [5], possibly because under nitrogen simultaneous nitride formation tends to block access to the silicon surface created by the devitrifying action of the metal. Although pre-nitridation treatments of silicon powder compacts under vacuum, or argon, are certainly feasible, a more simple procedure from the point of view of obtaining rapid reaction initiation might be the injection of a few vol% hydrogen into the nitriding gas during the furnace warming-up stage, nitridation being completed under 100% nitrogen. To what extent this type of two-stage process would affect the microstructure and properties of the resulting material needs to be investigated.

Subsequent to the reaction initiation stage the continuing presence of hydrogen in the nitriding atmosphere also gives rise to larger values of the reaction rate constants for both the α- and β-phase formation reactions compared with those for reaction in nitrogen alone. This second effect, the existence of which is apparent from the data of Dawson and Moulson [1], has now been studied in some detail [10] and the results will be published shortly.

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Surface energies of high explosives PETN and RDX from contact angle measurements

Recently, the fracture surface energies of PETN (pentaerythritol tetranitrate) and RDX (cyclotrimethylene trinitramine) have been determined by Hagan and Chaudhri [1], using a micro-indentation fracture mechanics approach. This technique involves measuring the work required to cleave a crystal creating two new surfaces and is advantageous because it provides the most direct determination of surface energy. Obreimoff [2] first reported the crystal cleavage method for measuring surface energy in experiments on mica. Later Gilman [3] added several refinements reducing uncertainty. However, the crystal cleavage method for obtaining surface energy has several difficulties.

The most serious problem with this technique is the irreversible nature of cleavage. Reversibility can only be approached for exceedingly low velocity crack propagation in an environment where gas adsorption does not occur. Plastic deformation and heat flow to the surroundings provide additional dissipative processes. To minimize the effect of dislocation motion some experiments have been done at cryogenic temperatures. Despite these difficulties, reasonably consistent results have been obtained [3] for a number of brittle materials, including LiF, MgO, CaF_2, BaF_2, and $CaCO_3$.

Another method for determining surface energy, involving contact angle measurements, has been described by Rhee [4]. The most common method for measuring the contact angle is the sessible drop technique [5]. In this experiment,