Letters

Effect of oxide impurities on the nitridation of high purity silicon

As part of a programme of work in this Department on reaction-sintered silicon nitride, a series of experiments were carried out, and have been reported in greater detail elsewhere [1], on the nitridation of high purity (99.999%) single crystal silicon in nitrogen atmospheres of carefully controlled purity. It was found that formation of the alpha and beta phases of silicon nitride, as determined by X-ray diffraction techniques, appeared to be influenced by the presence of trace impurities in the gaseous atmosphere, but in a sense opposite to that expected from information available on the effects of oxygen on phase stability in the system Si–N–O [2]. Under the best conditions obtainable with regard to nitrogen purity (oxygen 10^{-7} atm, water 2×10^{-6} atm) and using zirconium as a final getter, only the alpha phase was detected. When the zirconium was omitted and the oxygen and water levels raised to 10 to 20×10^{-6} atm, the thick films (5 to 15 μm) of nitride consisted of both alpha and beta phases in roughly equal amounts. Messier *et al.* [3] found that the use of tantalum or silicon getters in nitridations of silicon powder increased the proportion of beta phase, but runs made without getters resulted in specimens grossly contaminated with silica. This suggests that the background oxygen or water levels were far higher than in the present studies, and that the two sets of results are not comparable.

Continuation of work with single crystal material has now shown that the course of the reaction also appears to be sensitive to the type of alumina tubing (10 mm diameter, 100 mm long) used to contain the silicon, and zirconium getter. A nitridation temperature of 1375° C and a gas flow rate of 10 ml min^{-1} was used with times of the order of 20 h. The products of nitridations in tubes of sapphire or "Coram" (G.E.C. Ltd) contained 80% or more of the alpha phase. Nitridations under identical conditions in tubes of two types of commercial sintered alumina resulted in the formation of greatly increased proportions of the beta phase,

TABLE I

Inner tube	Experiment	Nitriding time (h)	Weight alpha nitride (% Si)	Weight beta nitride (% Si)	Mean total weight gain (% Si)	Mean percentages alpha nitride	Mean percentages beta nitride
Sapphire	31	6	4	0.2			
	32	15	6	0.5			
	41(a)	17	4	0.5			
	34	20	7	0.7			
	39(a)	20	5	1.0			
	33	48	5	0.2			
	Mean		5	0.5	5.5	91	9
Coram	37(b)	18	18	2			
	44(a)	19	7	2			
	35	20	8	1			
	38(b)	22	4	0.5			
	Mean		9	1.4	10.4	87	13
Alumina B	40	16	5	11			
	37(a)	18	5	6			
	36	20	2	4			
	39(b)	20	3	5			
	38(a)	22	2	3			
	Mean		3	6	9.0	33	67
Alumina A	41(b)	17	1	27	28.0	4	96

TABLE II

Inner tube	Experiment	Weight alpha nitride (% Si)	Weight beta nitride (% Si)
Sapphire	39	5	1.0
Alumina B		3	5
Sapphire	41	4	0.5
Alumina A		1	27
Coram	37	18	2
Alumina B		5	6
Coram	38	4	0.5
Alumina B		2	3
Coram	44	7	2
Coram + β-Al_2O_3		2	11

in one instance approaching 100% (Table I). The possibility of a direct effect on the course of these reactions of nitrogen purity, and of alumina itself, was excluded by carrying out simultaneous nitridations with two small tubes side by side in the reaction zone (Table II).

Analysis of these results shows that the amount of alpha phase produced is fairly constant over a range of conditions. The amount of beta phase varies considerably and depends on the type of alumina in use. Typical analyses [4] of sintered aluminas A and B are shown (Table III). In spite of attempted close control on nitridation conditions, even for the same type of alumina the amount of nitride formed tended to be erratic. Part of the variation may have been due to experimental errors arising from the small samples (10 to 20 mg) of silicon used in these studies, and the correspondingly small weight gains. A tendency for non-uniformity of growth of the nitride films may also have some responsibility, as may have variations in conditions within the outer reaction tube of alumina B. The overall extent of reaction in sapphire tubes appeared to be insensitive to time, and data from two runs of 6 and 48 h duration have been averaged in with the remainder.

The clear indication of these results is that remarkably small amounts of oxide or metallic impurity are able to determine whether predominantly alpha or beta silicon nitride is formed, apparently by accelerating the rate of beta formation, with the possibility of a corresponding slight diminution in the rate of alpha formation. Information already exists on the effects of large amounts of additive (NaF and AlF_3 for example [5], and Al [6] at the 2 to 3% levels) during the nitridation of silicon powders. It is also established that high percentages of certain oxides can be accommodated in both alpha and beta lattices without major change of crystal structure [7]. In these cases the unit cell dimensions are increased in proportion to the dissolved oxide, but a sample of beta "silicon nitride" containing even 1% of oxide would have its unit cell dimensions increased by only 0.01% and would be indistinguishable from pure nitride by X-ray diffraction. No departures from standard nitride lattice spacings were ever detected in the present work.

Even with nitrogen of high purity and in the presence of getters, it is impossible to eliminate completely the possibility of sample contamination when a conventional resistance heated alumina tube furnace is used. At 1375°C and considering separately the two simple dissociation processes:

$$Al_2O_3 \rightleftharpoons Al_2O + O_2 \quad (1)$$

$$Al_2O_3 \rightleftharpoons 2AlO + \tfrac{1}{2}O_2 \quad (2)$$

the equilibrium vapour pressures of Al_2O and AlO will be 5×10^{-15} and 2×10^{-14} atm respectively [8]. These values define approximately the theoretical limit of purity for the gaseous atmosphere. They are important in that they indicate that alumina at temperatures in the region of 1300 to 1400°C acts as a virtually limitless reservoir of oxygen and aluminium. In this work, however, other factors must be involved. It is known that at low oxygen partial pressures commercial sintered alumina tends to lose oxides (chiefly SiO, CaO, MgO, Na_2O and K_2O) on heating to temperatures in excess of 1100°C [9-12]. There appears to be a correlation between alumina purity and rate of beta silicon nitride production that is supported by the experiment carried out in a Coram tube in the

TABLE III

	% by weight Al_2O_3	SiO_2	Fe_2O_3	CaO	K_2O	TiO_2	Mn_3O_4	MgO	Na_2O	Cr_2O_3
Alumina A	99.4	0.01	0.09	0.07	0.02	0.02	0.01	0.19	0.13	0.03
Alumina B	99.7	0.10	0.08	0.03	0.02	0.01	0.01	0.01	0.01	0.01

presence of a small quantity (100 mg) of powdered beta-alumina ($Na_2O\ .\ 11Al_2O_3$) which slowly evolves sodium oxide at high temperature [13]. While the volatile alkali metal oxides, or the metals themselves, are likely contaminants, it is more difficult at this stage to be certain about which of the other impurities in the alumina could be involved. Steele and Williams [12] argue that both CaO and MgO would be appreciably volatile and, with an assumed partial pressure of oxygen of 10^{-18} atm, lead to vapour pressures of the metals in the region of 10^{-3} atm at 1300°C. Work is now in progress to determine the extent of pick up of metals by silicon under these conditions.

It is clear that under "high purity" conditions the alpha silicon nitride forming reaction tends to be kinetically highly favoured. It is also apparent that in some circumstances very small amounts of impurity can be more important in determining the alpha/beta silicon nitride ratio than the overall volume of oxygen in the system. The formation of the isostructural, and chemically similar beta germanium nitride in the nitridation of germanium powder [2, 14] also appears to be promoted by oxide impurities at certain concentrations.

The results of this work may help to explain the apparently favoured production of beta silicon nitride in the nitridation of silicon powder compacts at temperatures above the melting point of silicon [15]. The significant factor may not be a direct effect of temperature on reaction rate, or the appearance of liquid, but an increased rate of evolution of catalytic oxide impurities from furnace refractories. A further conclusion is that true beta silicon nitride will be very difficult to prepare in a state where it can be guaranteed that impurities are not a factor contributing to the stability of the phase, and until the role of trace impurities is better understood existing data on phase stability in the higher temperature regions may need to be treated with caution.

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On spiral eutectic growth

Spiral eutectic structures are relatively uncommon. They have been reported in the Al–Th [1] and in the Zn–Mg systems [2-4]. Recently, we reported some observations on spiral growth of the αAl–Mg_2Si eutectic [5] and discussed this growth in relation to instability behaviour of the Mg_2Si phase. Primary crystals of the latter, in the system investigated, grow as