The α/β-Si_3N_4 question

The recent lively discussion in this journal concerning the effects of hydrogen during the nitridation of silicon [1] and the complexities of formation of α- and β-Si_3N_4 during nitridation [2,3], demands further comment. It has been known since the inception of modern research on this question (the early work was carried out in the last century [4]) that there are no simple features which dictate either the formation of α or β. For example, both α or β form by solid state mechanisms during the nitridation of iron; α forms by a solid state crystallization of amorphous silicon nitride as low as 1250° C in impure samples [5] and as high as 1490° C when highly pure [5–7]. β forms in the solid state as low as 900° C from amorphous materials in the Si–C–N system produced by pyrolysis of methyl silicon imide [7], a finding confirmed by Jacobson, but at 1500° C, in amorphous material from silicon tetrachloride, ammonia and methane [8]. Most observers agree that α easily forms during nitridation of silicon by a vapour-phase mechanism clearly seen from the whiskery nature of much of the α; but, α also can appear as chunky, hexagonal prisms and platelets. β certainly appears as hexagonal prisms from molten silicon and can easily be distinguished by the lower angle of the (1 1 1) type cap faces as compared to the steeper (1 1 1) α faces (in accordance with the *c*/*a* ratios).

Unfortunately, β too can form by a vapour-phase mechanism and is especially noticeable in our recent work where 99.999%, 200 mesh, silicon powder has been heated rapidly to 1480° C in 90%N_2 + 8%H_2 + 2%H_2S. Fig. 1 shows the microstructure of the 98% β produced and, we suppose it represents vapour-phase deposition; it looks unlike the β normally produced from solid or liquid silicon. When 99.999% silicon is nitrided at ~ 1350° C, both α and β seem to occur in whiskery and more chunky morphologies.

In recent work we have discovered that sulphur greatly stimulates the nitridation of silicon, almost certainly by vapour-phase mechanisms involving SiS and SiS_2. No ternary Si–S–N compounds have been detected. SiS_2 and Si_3N_4 are compatible compounds. SiS_2 and SiS are deposited in cooler parts of the furnace, with Si (not silicon nitride!) from the disproportionation of amorphous SiS.

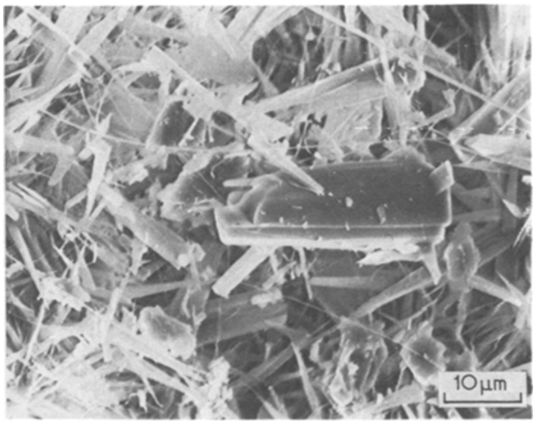

Figure 1 Sample of 98% β-Si_3N_4 suggesting vapour-phase transport to whiskers.

Boyer and Moulson [2] report that 99.999% silicon powder is 90% nitrided in 20 h at 1370° C in N_2 + H_2, while, in N_2 alone, only 30% converted. But, in 90%N_2 + 8%H_2 + 2%H_2S, 99.999%, 200 mesh silicon can be nitrided at 1280° C to completion in less than 12 h with a weight gain of ~ 40% and therefore little loss of SiS_x. A large number of runs has established this as being near to the optimal conditions. At this temperature S is undetectable by EDAX in the product, but in any case, annealing in a stream of N_2 + H_2 at high temperature removes traces of S by the removal of SiS_x. Firing in this atmosphere at temperatures < 1250° C produces large weight losses due to SiS_x distilling off.

Moreover, we have discovered that the whole question of the percentage of α or β formed during nitridation depends upon the pre-existing amount of α or β in the powder. α and β crystals grow competitively, probably partly by the *same* mechanism, including vapour-phase mechanisms, as they consume the available raw materials. For high α you simply start with some α seed and grow it. For β, you similarly "seed" with β in the classical chemical way.

The procedure was to carry out simultaneous runs in the following way in a two-tube furnace. Silicon powder in one tube is heated in hydrogen to the "seeding" temperature whereupon nitrogen (and sometimes H_2S) is carefully added for ~ 1 h. In the other tube, silicon powder remains in H_2. After "seeding", the nitrogen (and H_2S) is turned off and the tube flushed with H_2. The samples are

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TABLE I

"Seeding" temperature (° C)	Nitriding temperature (° C)	2% H_2S	α (%)	β (%)	Si left
–	1280	No	88	12	high
1390	1280	No	64	36	mod.
–	1280	Yes	96	4	0
1390	1280	Yes	33	67	0
–	1390	No	1	99	high
1280	1390	No	81	19	trace
–	1390	Yes	40	60	0
1280	1390	Yes	86	14	0

All "runs" 11 h; "seeding" 1 h. – denotes an unseeded run.

now heated, or cooled, to the "run" temperature in H_2 and then N_2 (and H_2S) carefully admitted for the 11 h run. After cooling in H_2, samples are cut and α/β ratios measured by XRD near the centre of the samples. No Si_2N_2O is seen. Preliminary runs, heating in H_2 to 1280 or 1390° C, and then admitting N_2 (and H_2S) showed that, at the former temperature, almost all α is produced; almost all β at the latter. Seeding at these temperatures, confirmed by XRD, produced $< 5\%$ α or β within the samples as desired; the initial phase of nitridation being slow. Subsequent runs at temperature then tend to produce more of the seeded phase at the expense of the other. Undoubtedly, seeding could also be done by simply ball milling silicon together with small amounts of α or β.

Table I illustrates these effects. It follows that when silicon is placed in N_2 (and H_2) and heated from room temperature to the operating temperature, as is most often done, the final α/β ratio will depend sensitively on the length of time that the silicon is in the lower temperature domain, 1000 to 1250° C, where α preferably forms. The fact that nitrided powder usually contains mostly α is due to this. Given no nitridation at lower temperatures, but heated in H_2 to 1390° C and then carefully nitrided, avoiding any exothermic melting, silicon powder can give 99% β with no microstructural evidence for liquid phase, (melting is quite easily spotted we find). As to other questions: speculation is too easy and plausible demonstration too difficult, as with the idea [3] of nitrogen diffusion down the *c*-axis "channels" of β. Fast ion diffusion is not simply related to the existence of so called "tunnels" or "channels" but is sensitively related to the nature of the walls of such channels. This includes the charge distribution, polarizability of "wall ions", chemical bond-type interactions and so on. There is no reason, given the strongly co-valently bonded nature [9] of the "channels" in β, to expect anything but extremely low diffusion values in β (or α); indeed, all evidence of sintering, etc. indicates this.

A further complication that all the previous observers have missed (astonishingly in view of the simple classical nature of the effect) is that α-Si_3N_4 will dissolve in liquid silicon and β reprecipitate, just as occurs in hot-pressed samples containing a liquid silicate phase. This can be simply demonstrated by partially nitriding silicon powder at ~ 1250° C to produce ~ 70% α, ~ 5% β, ~ 25% Si. If the sample is then heated to 1480° C in hydrogen (no nitrogen) for 6 h, very interesting effects are seen. Near the surface, silicon disappears (presumably by evaporation) and the sample is mostly α (as before) but, as the specimen is sectioned downwards, the percentage of silicon increases up to the same amount as in the original sample (25%) and, coincidentally, the percentage of β increases until the sample is 60% β, 15% α and 25% Si. Similar α/β ratio samples, but without free silicon, show no α/β change under the same treatment. Furthermore, if the 70% α, 5% β, 25% Si sample is heated to 1390° C in H_2, also no change in α/β ratio is detected. This shows that not only does α convert to β in liquid silicon, but that the rate and extent of conversion is directly related (of course) to the amount of liquid silicon present. This fact must greatly affect the growth morphology even under active nitridation. In addition, the effect may increase the size of flaws in material that has been nitrided above the melting point as the liquid silicon may move through the α matrix, consuming it and reprecipitating β.

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A note on the preparation of the high transition temperature superconductor lithium titanate

Superconductivity in $LiTi_2O_4$ was first reported by Johnston *et al.* [1] who also recognized this material as belonging to the cubic spinel group of compounds. These compounds are currently of much interest because they appear to be examples of a ternary system in which the superconducting property depends upon the strong coupling mechanism [2, 3]. Such materials are frequently difficult to prepare and our recent experience with $LiTi_2O_4$ indicates that this spinel is no exception, but that a single phased compound can be obtained provided certain conditions are satisfied. It is the purpose of this paper to describe circumstances which seem to provide these conditions and to briefly report the crystal structure and superconducting transition characteristics of the best material prepared by our method.

In the experiments carried out by Johnston *et al.* samples were produced by arc-melting Li_2CO_3, TiO_2 and Ti metal together, by sintering mixtures of $Li_2Ti_2O_5$ and Ti_2O_3 under a helium or argon atmosphere and by reduction of pre-reacted mixtures of Li_2CO_3 and TiO_2 with hydrogen. None of their procedures, however, produced single-phased material, some of the samples with highest superconducting transition temperatures apparently containing as much as 20% of unreacted $Li_2Ti_2O_5$ or other impurity.

In the present work therefore, efforts were directed towards a more detailed investigation of the best conditions for the following simple reactions:

(1) $Li_2CO_3 + 4TiO_2 + H_2\text{(gas)} = 2LiTi_2O_4 + CO_2\uparrow + H_2O\uparrow$

(2) $2LiH + 4TiO_2 + H_2\text{(gas)} = 2LiTi_2O_4 + 2H_2\uparrow$

The starting materials in each case were A.R. grade chemicals and the parameters investigated were sintering temperature and time at this temperature. For simplicity, all samples were mixed so as to yield a nominally stoichiometric product, hydraulically pressed to form a thin cylindrical pellet, and fired only once. However, subsequent investigation suggests that, unlike some other oxide spinels, repeated firing effects little improvement in either purity or stoichiometry. In all cases the firing run was arranged so that samples rose rapidly to the sintering temperature, were maintained at that temperature for a predetermined time, and then were furnace cooled. A continuous flow of hydrogen gas over the samples, held in a silica tube, was maintained throughout this programme.

In the experiments concerned with the effect