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Structural Nano-Defects in α-Silicon Nitride

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Abstract

Two types of α-silicon nitride powder have been examined by transmission electron microscopy. Clustered, nano-dimension, coffee-bean shaped features can be seen: these are believed to be dislocation loops. The features are concentrated towards particle centres and appear to be formed by the condensation of lattice point defects during cooling from powder production temperatures probably in the region of 1300 to 1500°C. Similar concentrations of features confirmed to be vacancy dislocation loops have been seen in the unconverted α-silicon nitride grains in hot-pressed silicon nitride. Calculations based on estimates of precursor defect concentrations suggest a very speculative value for the activation energy of formation of the Schottky type of lattice defect in α-Si_3N_4 of 670 kJ mol^{-1}.

1 Introduction

There has recently been considerable interest in the production of nano-dimension intragranular precipitates of silicon carbide within the silicon nitride grains of composite materials.[1] This work revives interest in the more general question of the possible defect nature of the silicon nitride crystal lattice, its capacity to accommodate localized structural defects, and in the nucleation and growth of second phases within the lattice. Ten years ago, Jack reported the observation of 25 nm intragranular, amorphous, disc-like, features in a black chemical vapour deposition (CVD) silicon nitride, which on annealing at 1850°C coalesced and then disappeared. It was postulated at the time that the discs were precipitates of amorphous silica.[2] More recently, internal microstructural features which were assumed to be nano-dimension copper- and tin-rich precipitates have been observed in grains of otherwise very high purity polycrystalline CVD α-silicon nitride; these features similarly disappeared after annealing at 1800°C.[3] Three recent publications[4-6] describe the observation of ~15 to 25 nm dimension dislocation loops in high purity CVD α-phase silicon nitride and in residual (untransformed) α-silicon nitride grains in hot-pressed or hipped silicon nitride. In the CVD materials the loops were characterized in some detail with respect to type, Burger's vector, and habit plane[4,5] The development of vacancy loops in the hot-pressed silicon nitride was attributed to the condensation of thermally activated vacancies during rapid cooling from densification temperature in the region of 1700°C.[6] It was assumed that any loops present in the starting (a high α-phase) powder would have been redissolved or annealed out during hot-pressing, and that those seen in the α-grains of the dense material had developed subsequently. However, since silicon nitride powder is itself produced at high temperature, followed by more or less rapid cooling to room temperature, it might be expected that the powder particles would contain their own populations of loops. Dislocation loops might therefore be a general feature of all rapidly cooled silicon nitride (and similar) materials.

The object of the work reported here was to extend the earlier high resolution transmission electron microscope (TEM) examinations,[6] in a search for similar structural features in silicon nitride powders. In this continuation study on two commercial powders we have observed moderately high densities of 'coffee-bean' nano-dimension features, which are postulated to be dislocation loops. The first powder from H.C. Starck (FRG) was produced by the nitridation of silicon powder at 1300 to 1400°C followed by mechanical milling to break down agglomerates;[7] the second was a high purity powder from Ube (Japan) produced by the lower temperature imide route followed by annealing at 1300 to 1500°C to crystallize the amorphous material.[8] Estimates of the point defect concentrations necessary to generate loops of concentration corresponding to the defects seen have been attempted.

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2 Experimental

Silicon nitride powders, H.C. Starck LC12N (specific surface area 17 $m^2 g^{-1}$, 96% α-phase, oxygen content 1.6%) and Ube E-03 B15X02 (specific surface area 3.2 $m^2 g^{-1}$, 95% α-phase, oxygen content 0.9%), were dispersed without preliminary treatment in isopropanol at 0.1 g dm^{-3} with 10 min ultrasonic agitation. A drop of suspension was dried on a 3 mm diameter copper grid, covered with Formvar polyvinyl, and ~3 nm carbon, films and examined in a Jeol 200 kV TEM/STEM microscope with a rotation angle of ±30°.

The dense hot-pressed silicon nitride reported on here had been formed by pressing Starck LC12N powder in a boron nitride lined graphite die at 1700°C under 20 MPa for 500 s. The densification aid consisted of 3% Al_2O_3 and 7% TiO_2 added to the powder as the metal alkoxides dissolved in isopropanol, followed by hydrolysis and drying at 120°C. On completion of the hot-pressing period the temperature fell by 200°C in the first 500 s of cooling and room temperature was reached in 2 h. X-ray diffraction analysis showed the material to contain ~70% of unconverted α-phase.

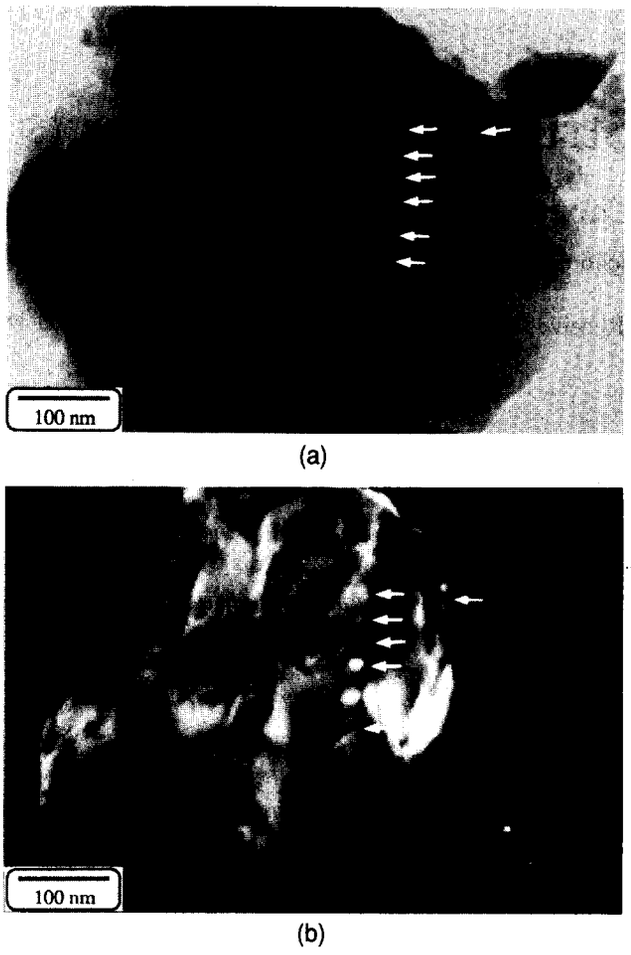

Fig. 2. Intragranular spherical features (arrowed) in a selected particle of H.C. Starck powder: (a) bright field; (b) dark field.

3 Results and Discussion

3.1 Powders

The two silicon nitride powders used were chosen because of their quite different production routes. The H.C. Starck powder had been subjected to milling, carrying with it the possibility of mechanically induced lattice strain and associated dislocation networks. This powder, while of small (~100 nm) mean particle size, had a relatively wide size range (Fig. 1), and the tendency for smaller particles to adhere to the larger made the observation of internal features in the smaller electron transparent particles difficult. Moreover, the larger particles, within which it would have been expected that most defects would be found, tended to be electron opaque. Therefore only a narrow range of particle sizes was in practice amenable to examination. Most particles picked out were additionally partially opacified by the presence of tangled dislocation networks, presumed to be the consequence of the post-nitridation milling. Randomly selected suitable particles were rotated to optimize the contrast of the characteristic coffee-bean strain fields of the defect features; dark field was used to aid confirmation of observations. Figures 2(a) and (b) show features, seen in bright field and dark field, in particles of Starck powder. Unambiguous identification of the nature of the internal features seen (vacancy or interstitial loop, or precipitate) was impossible because of the size of the larger particles (500 nm) which did not lend themselves to high resolution microscopy, and the disturbance of contrast caused by the attached smaller particles. It is believed, however, because of their transparency to the electron beam and on the basis of previous observations made using high resolution TEM with the positive identification of missing lattice planes,[6] that they may be vacancy loops.

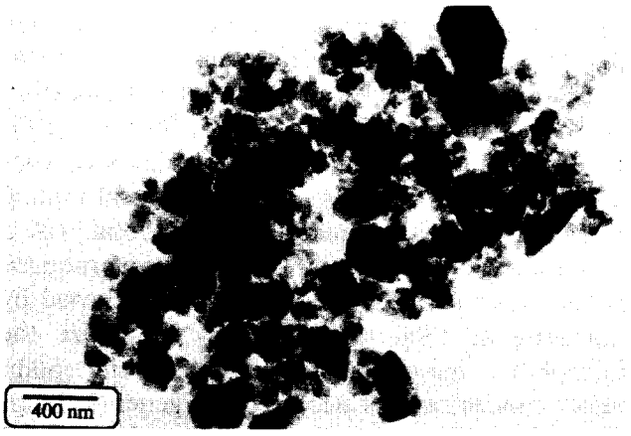

Fig. 1. H.C. Starck powder: general overview showing the wide particle size range.

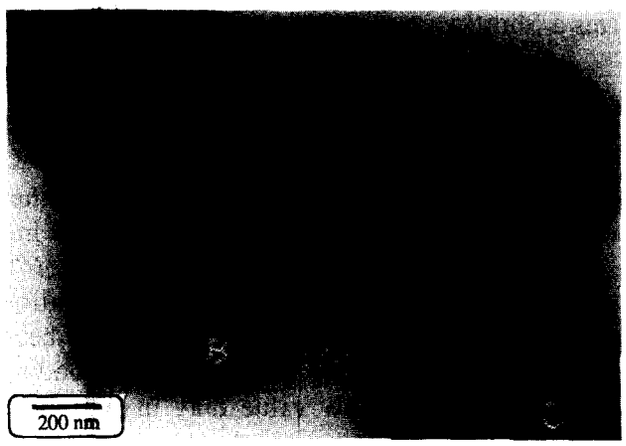

Fig. 3. Three UBE powder particles at low magnification, showing typical features under bright field.

The Ube powder particles were more easy to examine because of their narrow size range and uniformity of particle shape, although the range of picture contrast obtainable was narrow because of the particle thickness. Because their production route did not involve milling it was considered that there was a much greater chance that they would be strain-free. Internal 10 to 30 nm dimension strain centres similar in every respect to those seen previously exist also in these particles, three of which are shown in Fig. 3. Figures 4(a) and (b) show in higher magnification the features of particle A in bright and dark field; Figs 5(a) and (b) similarly show those in particle C. As with the Starck powder, the degree of resolution possible with samples of such thickness makes positive identification of their nature impossible; however, it is suggested that they are vacancy dislocation loops, for the reasons given above, and because of the likelihood that the formation of vacancy (rather than interstitial) point defects will be intrinsically energetically more favourable in the largely covalent silicon nitride.

We therefore suggest that nano-dimension precipitates or dislocation loops are a normal feature of α-silicon nitride grains and particles, and a consequence of the standard quite rapid cooling from fabrication temperature, resulting in the sudden development of supersaturated concentrations of point defects. A common feature in the two types of powder particles, as with the dislocation loops in the hot-pressed silicon nitride grains, is the existence of a defect-free zone at the particle perimeter, here of about 75 nm width and seen most clearly in Fig 5(b). This suggests that in all cases the features have formed by the condensation of high concentrations of a lattice defect which is partially able to escape by diffusion to grain

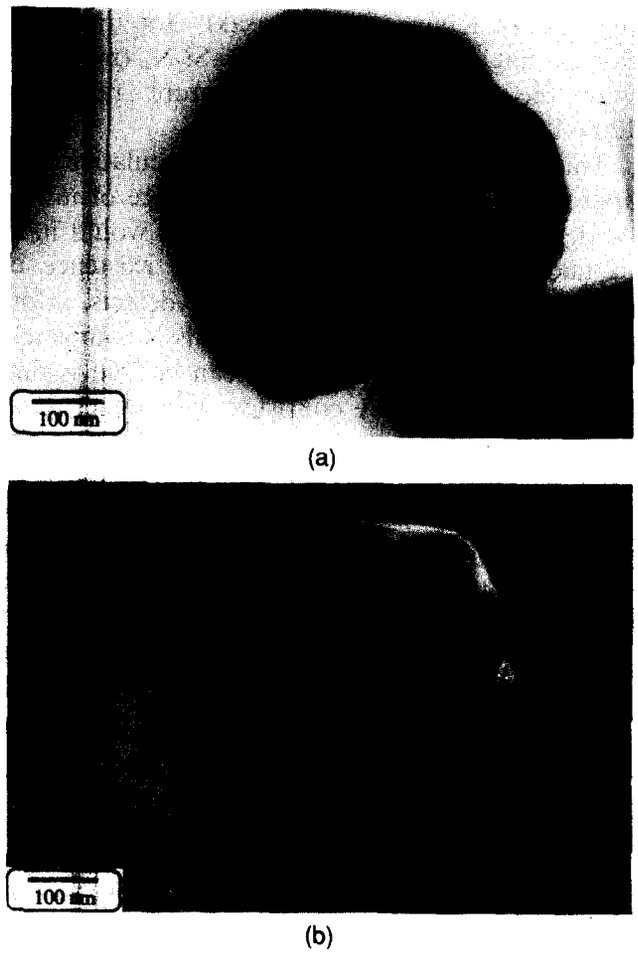

Fig. 4. UBE particle A at higher magnification: (a) bright field; (b) dark field.

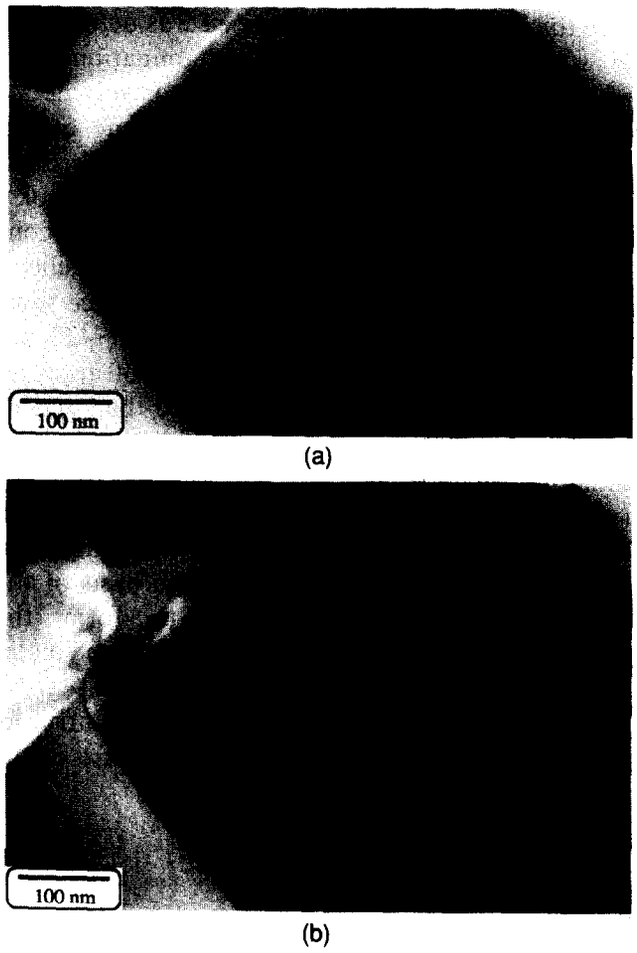

Fig. 5. UBE particle C at higher magnification: (a) bright field; (b) dark field.

boundaries or particle surfaces. If the powder features are dislocation loops they would be likely to redissolve or be annealed out during heating (for an hour or more) at sintering temperature, although to secure absolute proof of this would require more precise information about vacancy mobility in silicon nitride at these temperatures. On the basis of the width of the defect-free zones measured earlier,[6] and using the Einstein–Smoluchowski relationship, the very approximate value of 2×10^{-18} m^2 s^{-1} at ~1700°C was estimated for the silicon nitride 'vacancy' diffusion coefficient in α-Si_3N_4.

3.2 Hot-pressed material

It is possible to try to quantify the point defect concentration required for the precipitation of the dislocation loops in the α-Si_3N_4 grains of the hot-pressed material. For simplicity it is assumed that the condensation of thermally activated point defects is solely responsible for the formation of the dislocation loops, and that all the vacancies present further than ~50 nm from the grain surface form loops. Examination of an α-Si_3N_4 grain section of area 700 x 130 nm^2 in a thinned foil of hot-pressed silicon nitride showed 62 loops of diameter ~25 nm (the grain was rotated to ensure that all the loops within this area were counted). The thickness of the foil examined was determined *in situ* using the standard contamination spot technique[9] to be 175 nm, giving a volume of examination of 0.0159 μm^3. The volume of the unit cell of α-Si_3N_4, which contains four formula units, is 0.293 nm^3 (Ref. 3) and, following Brook[10] and assuming that an Si_3N_4 'vacancy' ($V_{Si_3N_4}$) consists of a Schottky type of defect with three silicon ($V_{Si}^{''''}$) and four nitrogen ($V_{N\cdots}$) vacant lattice sites, the mean linear dimension for $V_{Si_3N_4}$ is ~420 pm (indicating that the average loop disc of approximate volume 206 nm^3 should require the condensation of ~2800 $V_{Si_3N_4}$). An estimate for the minimum Schottky defect concentration [$V_{Schottky}$] (where the square brackets are used to indicate a fractional concentration) at the hot-pressing temperature of 1700°C, calculated on the basis of the volume of vacancies required to form the number of loops divided by the volume of material in which they were counted, is thus 8×10^{-4}. Assuming that the vacancies are entirely intrinsic, thermally activated defects and making use of the relationships

$$0 = 3[V_{Si}^{''''}]+4[V_{N\cdots}] \quad (1)$$

where

$$[V_{Si}^{''''}] = 3\,[V_{Schottky}] \quad (2)$$

and

$$[V_{N\cdots}] = 4\,[V_{Schottky}] \quad (3)$$

gives a Shottky equilibrium constant (K_s) of:

$$K_s = 3^3 \times 4^4 \times [V_{Schottky}]^7 \quad (4)$$

or

$$K_s = 6912\,[V_{Schottky}]^7 \quad (5)$$

and ~ 1×10^{-18}. On the assumption as before that precipitation of the loops occurs rapidly after initiation of cooling from 1700°C, $\Delta G_{Shottky}$ is ~670 kJ mol^{-1}. This value for the Schottky formation energy is perhaps not as high as might have been expected, given the strong and directional bonding of silicon nitride: a low value may in part be a result of the strain energy of the α-silicon nitride lattice, although the disorder entropy term arising from the seven vacant atomic lattice sites must also be a favouring factor.

On the basis that the rate-controlling step in the diffusion of the Si_3N_4 'vacancy' is that of the slowest species, believed to be N,[11] a very approximate estimate can also be made for the self-diffusion diffusion coefficient for N (D_N) in the α-Si_3N_4 grains at the hot-pressing temperature (1700°C). This is calculated using the relationship $D_N = 4D_V[V_{Si_3N_4}]$, setting $D_V \approx 2 \times 10^{-18}$ m^2 s^{-1} on the basis of the width (~20 nm) of the defect-free zone and $[V_{Si_3N_4}] = 8 \times 10^{-4}$, to give $D_N \approx 6 \times 10^{-21}$ m^2 s^{-1}. This value compares reasonably well with that of 10^{-19} m^2 s^{-1} estimated by extrapolation of the data of Kijima and Shirasaki[11] for ^{15}N diffusion in single crystal grains of α-Si_3N_4 (measured over the much lower temperature range of 1200–1410°C).

This analysis, which is both speculative and approximate, assumes only the presence of intrinsic defects; a more realistic treatment would need to take into account the probable existence of extrinsic, impurity generated, point defects, information on which for these materials is completely lacking. Perhaps the least that can be said is that the values derived are consistent with other data, but it is clear that a more complete study of the defect chemistry of silicon nitride is needed, focusing on the influence on atomic mobility of low concentrations of metallic impurity elements. The failure so far to detect dislocation loops in grains with the β-Si_3N_4 structure may be a result of higher atomic diffusivities in a lattice containing high concentrations of extrinsic defects associated with impurity atoms.

4 Conclusions

Distinctive nano-dimension 'coffee-bean' strain centres associated with structural defects appear to be a normal feature of α-Si_3N_4 grains and powder particles. While some may be associated with

impurity precipitates, those seen in the hot-pressed Si_3N_4 grains examined here are believed to be vacancy dislocation loops, condensing (most probably during rapid cooling from production temperature) in a lattice which is supersaturated with respect to Schottky defects. Very approximate estimates of the Schottky defect concentration at 1700°C and of the defect formation energy, made on the basis of dislocation loop densities in the α-Si_3N_4 grains of a hot-pressed material, are 8×10^{-4} and 670 kJ mol^{-1} respectively.

It is recognised that these are very tentative values, based on a speculative approach; it is hoped that this brief study will serve to stimulate more work on the subject.

Acknowledgements

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