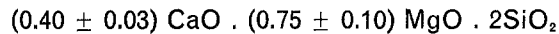


The identification of a grain-boundary phase in hot-pressed silicon nitride by Auger electron spectroscopy

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The presence of magnesium, calcium and oxygen has been detected in the intergranular fracture surface of an Si_3N_4 -7% MgO hot-pressed material by Auger electron spectroscopy, together with a chemical shift in the silicon Auger peak. The composition of this grain-boundary phase has been estimated as



by comparison with spectra obtained from a bulk glass specimen of similar composition. The reduction in strength of the hot-pressed material at temperatures above 1000°C has been attributed to the decrease in viscosity of this phase.

1. Introduction

A recent paper by Drew and Lewis [1] reported the observation by transmission electron microscopy of an amorphous phase present between the grains of β - Si_3N_4 in material hot pressed from α - Si_3N_4 with the addition of 7% MgO. A similar observation has also been reported by Kossowsky [2]. The present paper is concerned with an analysis of this grain-boundary phase by Auger electron spectroscopy (AES). AES was used in this instance as previous attempts to identify the phase by selected-area diffraction and X-ray microprobe analysis had not been successful. The advantage of AES is that it is extremely surface sensitive, analysing only the top two or three atom layers and so can be very powerful in certain circumstances. A comprehensive review of AES has recently been published by Riviere [3]. In the present study, scanning electron microscopy indicated that the hot-pressed material fractured intergranularly at temperatures in the region of 1200°C ; therefore, it was decided to attempt to analyse a fracture surface by AES and compare this

analysis with one obtained from the bulk material.

2. Experimental

The material used to make the specimens for the investigation was fully transformed from α - to β - Si_3N_4 by hot pressing at 1700°C for 1 h at 3.15 kg mm^{-2} . The α - Si_3N_4 had been made by nitriding silicon powder. Two typical chemical analyses of the impurities present in the starting silicon powder are shown in Table I. The fracture surface to be analysed was fractured by three-point bending at 1200°C in the atmosphere. A bulk specimen for purposes of comparison was prepared by ion beam machining with 5 kV argon ions incident at 40° to a surface rotating at 15 rpm. The specimens were loaded into the Auger apparatus together and the vacuum chamber pumped down to a background pressure of 2×10^{-10} Torr after a 24 h bake at 250°C . The surfaces of the specimens were then analysed using a commercial hemi-cylindrical electron velocity analyser. The surface to be analysed was positioned normal to the axis of the analyser and

TABLE I Chemical analyses of the impurities present in the starting silicon powder

Impurity (at. %)						
Al	Cu	Fe	Ni	Mn	Cr	Mo
(1) 1.07	0.33	0.82	0.006	0.022	0.020	—
(2) 0.90	0.27	2.06	0.11	0.031	0.069	0.05

the primary electron beam was incident at 16° to the surface normal. Contamination of the specimen surface due to exposure to the atmosphere was removed by bombarding with 500 eV argon ions with an ion density of about $1 \mu\text{A cm}^{-2}$ in a pressure of argon of 5×10^{-5} Torr. Auger analyses were performed without pumping away the argon but with the argon ion gun switched off.

3. Results

The spectra for the as-loaded ion beam machined surface showed mainly a very large carbon peak and some oxygen and other trace contaminants. However, the fracture surface showed a large oxygen peak, probably due in part to oxidation of the fracture surface as it fell out of the high temperature fracture stage, small silicon and nitrogen peaks, a carbon peak and also a small peak at 290 eV. After ion bombarding, the ion beam machined surface started charging and the incident beam energy had to be progressively reduced and the electron gun slightly defocused in order to prevent this. Several hours bombarding was required before the carbon peak was reduced to a minimum value which was constant with further bombarding, and a typical spectrum is shown in curve 1 of Fig. 1. By comparison a spectrum from the fracture taken under similar conditions is shown in curve 2 of Fig. 1. This spectrum was taken after an estimated 30 Å had been removed from the surface. Comparing the two spectra in Fig. 1 it can be seen that the silicon peak from the fracture surface is considerably altered in shape and has been shifted to lower energy by about 8 eV. The peak at 290 eV on the fracture surface has grown and can be identified as calcium. The oxygen peak is much bigger than that on the ion beam machined surface whereas the nitrogen peak is much smaller. The ion beam machined surface also shows a small peak at 47 eV which has been attributed to iron, a known impurity in the starting material, and a peak due to argon probably implanted during the ion beam machining. The fracture surface did not suffer from charging to the same extent as the ion beam machined surface and a typical spectrum taken at a higher incident beam energy is shown in Fig. 2. In this spectrum a high energy peak due to magnesium could also be detected and in the low energy silicon peak a minimum could be resolved at the position of the bulk silicon peak. Ion bombarding to remove a further 30 Å from the

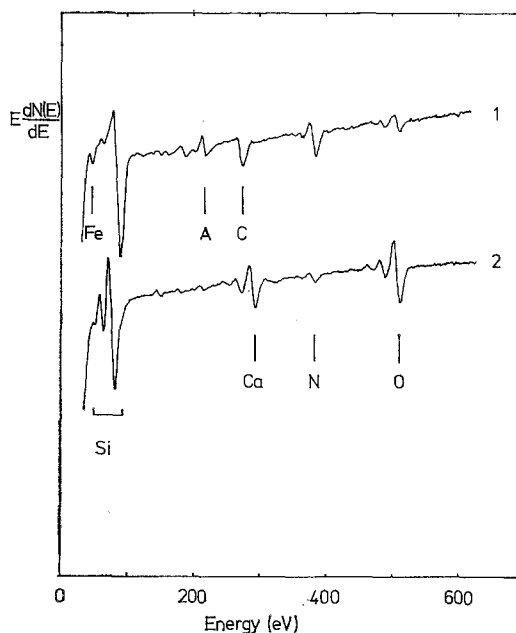


Figure 1 Auger spectra from hot-pressed silicon nitride: 1. Ion beam machined surface, incident electron energy 1.0 keV, modulation on analyser 3.5 V peak to peak (p-p). 2. Fracture surface, incident beam energy 1.2 keV, modulation on analyser 3.5 V p-p.

fracture surface produced no marked changes in this spectrum but there was a small decrease in the relative heights of the calcium and magnesium peaks.

4. Discussion

The presence of significant amounts of calcium, magnesium and oxygen on the fracture surface, together with the transmission electron microscope observations [1], suggest that the grain-boundary phase is a glass containing silicon, magnesium and calcium oxides. If this is the case the shift and change of shape of the low energy silicon Auger peak is to be expected due to the change in chemical environment of the silicon atoms. The Auger peaks due to silicon in the region below 100 eV involve transitions from the valence band, and Maguire and Augustus [4] have shown that changes in the density of states of the valence band are reflected in the Auger spectrum. Thus the main Auger peak from a nitrated silicon surface has been reported to be at 86 eV by Heckingbottom and Wood [5] whereas the main peak in pure silicon is at 91 eV. Similarly, oxidation of silicon [6, 7] causes the main peak

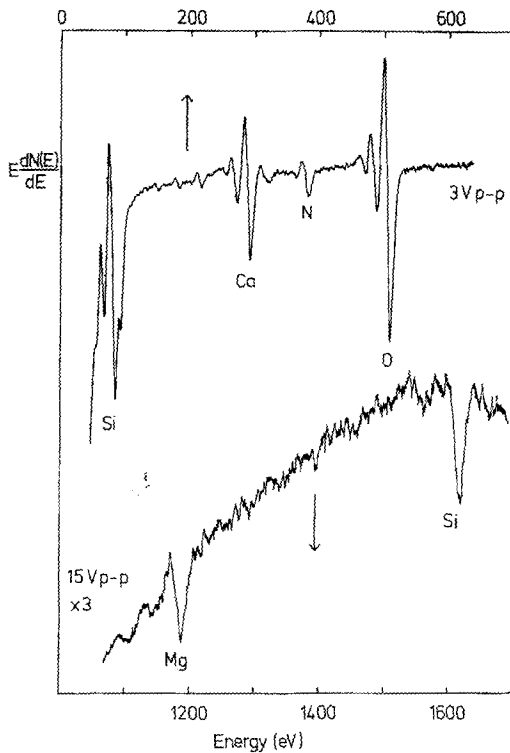


Figure 2 Auger spectrum from the specimen fractured at 1200°C . Incident electron energy 2.5 keV.

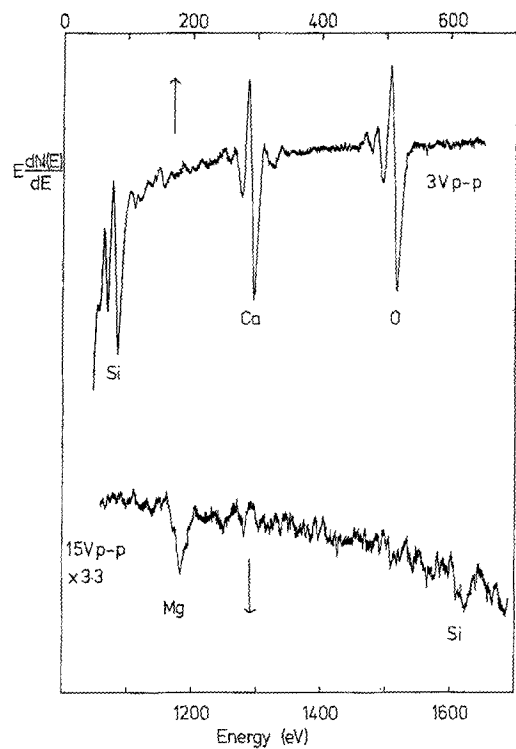


Figure 3 Auger spectrum from the CaO.MgO.2SiO_2 glass surface. Incident electron energy 2.8 keV.

to shift to about 75 eV with a much greater change in peak shape. In view of these results and in an attempt to make the analysis of the grain-boundary phase more quantitative it was decided to make a bulk glass specimen for purposes of comparison. The ternary phase diagram for CaO-MgO-SiO_2 [8] shows a region of low melting point about the composition CaO.MgO.2SiO_2 so a glass of this composition was prepared by inductively heating the components in an iridium crucible under 5 atm helium pressure and pouring the melt onto a cool plate. A typical spectrum obtained from the surface of this glass after it had been ion bombarded to remove contamination is shown in Fig. 3. Immediately it can be seen that the position and shape of the silicon peak on the glass surface is very similar to that obtained from the fracture surface. The calcium and magnesium peaks are also much the same except that their intensity relative to the silicon peaks is somewhat larger. Assuming that the Auger peak height in the differential spectrum is proportional to the concentration of the element in the surface, that

there is no preferential removal of one element by the ion bombardment and that the grain-boundary phase is thick enough to be considered as bulk material from the point of view of the Auger electrons, we can obtain an estimate of the composition of the grain-boundary glass by comparing spectra from the fracture surface and the glass specimen taken under similar conditions. The mean values obtained from spectra taken on different areas of the fracture surface and after different amounts of ion bombardment is: $(0.40 \pm 0.03) \text{CaO} \cdot (0.75 \pm 0.1) \text{MgO} \cdot 2\text{SiO}_2$. From the phase diagram [8] the melting point of this compound is about 1650°C but the mean value falls in a region where the melting point is changing very rapidly with composition and the error limits include compositions whose melting points are well below 1500°C . Thus it would seem reasonable to attribute the rapid reduction in strength of this material between 1000 and 1400°C [9] to the softening of the grain-boundary glass phase. Indeed, the data presented by Turkdogan and Bills [10] show that the viscosity of a glass of this composition is

decreasing rapidly in this temperature range, from a value of 600 P at 1200°C to about 50 P at 1400°C. The viscosity of CaO–MgO–SiO₂ glasses also reduces rapidly with increasing CaO plus MgO content, an increase from 20 at. % (CaO + MgO) to 30 at. % (CaO + MgO) reduces the viscosity at 1200°C from 1.5×10^5 P to 3×10^3 P.

Kossowsky [2] came to a similar conclusion analysing surfaces by AES from hot-pressed Si₃N₄ with MgO as additive fractured at room temperature in UHV. His estimated analyses, obtained by a rather less direct method, show somewhat less CaO and MgO in the grain-boundary phase but he makes no mention of a change in the silicon peak shape and position on the fracture surface so it is not clear how much of the surface is in fact intergranular in this case.

Kossowsky also concludes that there is a considerable amount of nitrogen in the grain-boundary phase whereas our data would suggest that any nitrogen we see in the fracture surface could be explained by a fraction of the exposed surface being β-Si₃N₄, particularly as we can resolve a silicon peak on the fracture surface in the position characteristic of the bulk material.

The viscosity data [10] show that MgO and CaO are equally effective in reducing the viscosity of CaO.MgO.SiO₂ glasses so it is not immediately obvious why the presence of calcium as an impurity has such a marked effect on the strength properties, whereas the amount of MgO additive has relatively little. The most reasonable explanation would seem to be that the concentration of MgO in the glass phase is approximately constant, whereas any calcium impurity all goes into the glass phase and increases the total CaO + MgO concentration.

This hypothesis is supported by the data of Kossowsky [2] from two fracture specimens with varying amounts of calcium and by the suggestion of Oyama and Kamigaito [11] that magnesium can substitute into the β-Si₃N₄ lattice whereas calcium would not be expected to.

5. Conclusions

The intergranular amorphous phase in silicon nitride hot-pressed with 7% MgO has been identified as a glass having the estimated composition

$(0.40 \pm 0.03) \text{CaO} \cdot (0.75 \pm 0.10) \text{MgO} \cdot 2\text{SiO}_2$.

The rapid decrease in the strength of this material at temperatures above 1000°C has been attributed to the decrease in viscosity of this glass phase.

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Received 13 June and accepted 2 July 1974.