Growth of $\beta$-Silicon Carbide on Silicon

BY A.S. BROWN* AND B.E. WATTS

Allen Clark Research Centre, The Plessey Company Limited, Caswell, Towcester, Northants, England

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The structure and topography have been examined of $\beta$-SiC layers formed on silicon heated in a low pressure of ethylene in an ultra-high vacuum system. Particulate epitaxic growth has been observed on substrates of various low-index orientations and an unusual double epitaxic relationship on (110) substrates noted.

Introduction

Thin oriented films of cubic $\beta$-silicon carbide have been grown on silicon substrates by the reaction of hydrocarbons with silicon under high-vacuum conditions (Khan & Summergrad, 1967) as well as in conventional gas-flow systems where the hydrocarbon is mixed with an inert carrier gas (Nakashima, Sugano & Yanai, 1966; Spitzer, Kleinman & Frosch, 1959) or where the silicon is heated in the presence of graphite (Tombs, Comer & Fitzgerald, 1965). The formation of $\beta$-SiC due to residual contamination (Newman & Wakefield, 1960; Rovida & Zanazzi, 1968) has also been detected on specimens heated in vacuum. We have examined the structure and topography of epitaxic $\beta$-SiC formed on single-crystal silicon substrates by heating at various temperatures in ethylene at $2 \times 10^{-6}$ torr in an ultra-high vacuum system. An unusual epitaxic relationship on (110) substrates is reported.

Experimental

The substrates used were in the form of bars approximately $20 \times 6 \times 1$ mm cut from a single-crystal boule of silicon (resistivity $\sim 50$ ohm cm, p-type boron doped) so that the two largest faces were within 1° of a low-index plane, either $\{100\}$, $\{110\}$, $\{111\}$ or $\{311\}$. One of these faces on each substrate was then lapped, mechanically polished and finally gas polished with HBr vapour in hydrogen at $1200^\circ$C.

In order to produce substrates comparable with those used by Khan & Summergrad (1967) a few specimens were chemically polished with an HNO$_3$–3%HF solution after mechanical polishing.

Immediately before use, the substrates were etched in HF solution for 30 minutes, quenched with methanol and then rinsed in deionized distilled water. Each bar was then mounted in an oil diffusion pumped ultra-high vacuum system in tantalum clips supported on high-current feedthroughs, allowing specimen heating to be carried out as required by passing a low-tension current through the bar after initial 'starting' at mains voltage (240 V). The system was then pumped down with overnight bakeout at $250^\circ$C to better than $5 \times 10^{-10}$ torr.

Prior to growth, the silicon bar was outgassed at 200–400°C for 40 minutes. Research grade (99-9% pure) ethylene from an all-metal pumpable gas-handling line was then introduced to an indicated pressure of $2 \times 10^{-6}$ torr. The sample was then heated for 10 to 90 minutes at temperatures between 800 and $1250^\circ$C observed with a disappearing-filament pyrometer corrected for emissivity (Allen, 1957). A number of specimens were thermally cleaned prior to growth by heating to $1230^\circ$C for 10 minutes in ultra-high vacuum after the outgassing stage (Joyce, Neave & Watts, 1969; Charig & Skinner, 1969). Samples were also heated at typical growth temperatures in the absence of ethylene both with and without prior thermal cleaning.

Substrates treated as described were all examined by glancing angle electron diffraction using 75 kV electrons at an incidence angle of less than 1°. Thinned specimens were also examined by transmission electron microscopy in a Siemens Elmiskop I using 100 kV electrons. Transmission electron micrographs were also taken from replicas which were prepared by evaporating platinum–carbon onto the surface at an angle of about 10° followed by stripping from the substrate by immersion in 18:1 HNO$_3$:HF.

Results

On the substrates exposed to ethylene at temperatures between 800 and $1150^\circ$C, the silicon carbide detected by glancing angle electron diffraction was always the

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* Present address: Northern Electric Research and Development Laboratories, P.O. Box 3511, Station C, Ottawa, Ontario, Canada.
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cubic modification, $\beta$-SiC, and was usually epitaxic, with very little polycrystalline material detectable. Samples heated in the same temperature range in the absence of ethylene also showed detectable amounts of epitaxic $\beta$-SiC unless previously thermally cleaned. No $\beta$-SiC formation was detected on any of the specimens heated in ethylene or in vacuum above about 1190°C.

On (100), (111) and (311) substrates the predominant orientation of the epitaxic material was parallel with that of the substrate (i.e. (100) $\beta$-SiC parallel to (100) Si with [110] $\beta$-SiC parallel to [110] Si). The glancing angle electron diffraction pattern from growth at 1050°C on a (111) substrate is shown in Fig. 1. On (110) substrates a second epitaxic relationship was found in addition to the expected parallel orientation which had (111) $\beta$-SiC parallel to (110) Si with [112] $\beta$-SiC parallel to [001] Si. Some twinning of the $\beta$-SiC about (111) axes was observed on substrates of all orientations and double positioning was present in parallel growth on (111) substrates as well as in non-parallel growth on (110) substrates.

The proportions of the two orientations on (110) substrates were dependent upon substrate temperatures. At the lowest growth temperatures (830–900°C) the non-parallel epitaxic relationship predominated. Increasing proportions of the parallel orientation were observed in the temperature range 900–1000°C while at higher temperatures (1000–1140°C) the (110) $\beta$-SiC orientation predominated. Fig. 2 is the glancing angle electron diffraction pattern from growth on (110) silicon at 950°C; i.e. in the intermediate temperature range, and shows both $\beta$-SiC orientations present.

No significant differences were observed between deposits on gas polished and chemically polished specimens, particularly with regard to the presence of two epitaxic relationships on the (110) surfaces at lower temperatures.

Transmission electron micrographs of a range of specimens showed that the epitaxic silicon carbide growth on all orientations was in the form of discrete particles and stereo-pair micrographs demonstrated that these particles were all at the silicon surface. Pt-C replicas also showed the particulate growth since carbide particles were extracted from the surface by the replication technique (Smith & Nutting, 1956). Fig. 3 is a replica transmission electron micrograph of growth on a (111) substrate and shows carbide particles formed both inside and outside the shallow triangular etch pit areas on the surface. Etch pits were observed on substrates of all orientations heated between about 950 and 1050°C irrespective of the presence of ethylene, unless the substrate had been previously thermally cleaned. They were roughly triangular on (111) substrates and roughly hexagonal on (110) substrates. On the other orientations their geometry was ill-defined. The silicon carbide particles formed on thermally cleaned substrates (Fig. 4) were considerably larger and at lower number density than those formed under comparable growth conditions on substrates which had not been thermally cleaned.

**Discussion**

Two salient features emerge from the above work: firstly that thin $\beta$-SiC layers (<1000 Å) grown in an ultra-high vacuum system using low partial pressures of ethylene are discontinuous and, secondly, that an epitaxic relationship exists between $\beta$-SiC and silicon which has not been previously reported. The particulate growth of $\beta$-SiC has been observed by Newman &

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Fig. 2. Electron-diffraction pattern of $\beta$-SiC on (110) Si, 950°C growth, beam in [001] Si direction.

Fig. 3. Replica transmission electron micrograph of $\beta$-SiC grown at 1025°C on (111) Si.
Wakefield (1964) on substrates heated in poor vacuum, who also noted the formation of etch pits under these conditions.

The specimens as introduced into the system have been shown by Auger electron spectroscopy (AES) to have a coverage of hydrocarbon or other carbon-containing species (Charig & Skinner, 1969) and in fact detectable amounts of β-SiC were observed on specimens heated at between 830 and 1050°C in ultra-high vacuum. The marked difference in the morphology of the β-SiC deposited after thermal cleaning could thus be related to surface cleanliness. The absence of detectable β-SiC growth at temperatures above 1190°C could also be due to a thermal cleaning process as well as a possible reduction in sticking probability for ethylene at higher temperatures.

Substrate etching is probably an effect of the residual oxide film present on the substrate as inserted in the system (Charig & Skinner, 1969) as a result of loss of silicon by evaporation as silicon monoxide, but the presence of surface contamination would also appear to be necessary for discrete etch pit formation. As both oxide and carbon contamination are rapidly removed during thermal cleaning, no etch pit formation during subsequent β-SiC growth would be expected.

It appears that lattice matching could account for the existence of the second non-parallel epitaxic relationship on (110) substrates. In the parallel relationship the lattice mismatch is about 20% in both the [T10] and [001] directions. In the non-parallel relationship the lattice mismatch in the [T10] direction is retained but becomes about 2% in the substrate [001] direction. Although matching is not close in either case, a better fit is achieved in the non-parallel orientation and this orientation is favoured at lower temperatures. At the higher temperatures correlation of symmetry elements apparently predominates over lattice matching considerations (Pashley, 1965).

Conclusions

It has been shown that particulate epitaxic growth of β-SiC results when single-crystal silicon substrates are heated to temperatures between 830 and 1140°C in 2×10⁻⁶ torr of ethylene in an ultra-high vacuum system. Epitaxic β-SiC has also been found on substrates heated in the same temperature range in ultra-high vacuum, owing to a residual contamination of the silicon surface which can, however, be removed by prior thermal cleaning at 1230°C. No α-SiC was observed on any substrate treated as described.

On (111), (100) and (311) substrates a parallel epitaxic relationship has been shown to exist between the β-SiC deposit and the substrate. On (110) surfaces, however, an additional epitaxic relationship has been observed.

Fig.4. Replica transmission electron micrograph at β-SiC grown at 910°C on thermally cleaned (111) Si.

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