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EPITAXIAL GROWITH OF β-SiC THIN FILMS ON 6H-SiC SUSBTRATES USING THE SOULTION PRCURSOR METHOD

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Epitaxial Growth of β-SiC Thin Films on a 6H-SiC Substrate Using the Solution Precursor Method

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Abstract

A polyvinylmethylsilane precursor has been used for the epitaxial growth of SiC thin films on 6H-SiC single crystal substrates. The films were prepared by dipping the single crystalline 6H-SiC substrates into the precursor polymer solution with subsequent thermal treatments at different temperatures. Transmission electron microscopy (TEM) was used to characterize the microstructure and chemistry of the different SiC films. At 1100 °C, the film was amorphous and contained substantial oxygen. At 1600 °C, an epitaxial, single crystalline β-SiC film was observed.

1. Introduction

Silicon carbide (SiC) single crystal thin films have received attention for temperature stable, p-n junction-diodes, field effect transistors, and blue light-emitting diodes [1, 2, 3]. An economic and useful method to grow epitaxial thin films is by the thermal decomposition of suitable precursors at high temperatures [4]. Polymer precursor chemistries, that are liquid at room temperature, have been used for the manufacturing of non-oxide ceramic monoliths [51, fibers [61 and coatings [7]. Typically, the polymer precursor is shaped in the liquid state as, e.g., fibers, thin films, and then decomposed (pyrolyzed) to synthesize the inorganic, e.g. Si3N4, SiC- In this work, the polymer precursor is used to produce a single crystal thin film via an epitaxial process on a single crystal SiC substrate by heat treating the pyrolyized precursor at higher temperatures.

2. Precursor Synthesis

The polyvinylmethylsilane precursor was synthesized by dissolving dichloromethylvinylsilane (0.77 mol), dichlorodimethylsilane (0.41 mol) and chlorotrimethylsilane (0.39 mol) in a toluene (500 ml)/tetrahyrofurane (50 ml) mixture [8, 9]. Reaction with sodium (2.8 mol) at 100 °C results in the formation of soluble (70 81 %) and insoluble (19 - 30 %) products. After filtration and subsequent removal of the solvent a viscose yellowish oil was obtained. The average molar

weight of the polyvinylmethylsilane was measured by gel-permeation-chromatography to be -3076 g/mol [8]. The chemical structure of the polyvinylmethylsilane precursor is suggested by the schematic shown in Fig. 1. Pyrolysis of the polysilane oil in argon at 1100 °C (heating rate: 1 K/min) leads to the formation of a ceramic residue with the composition given in Table 1. The ceramic yield after the pyrolysis was approximately 45 wt%.

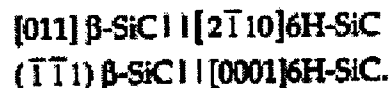
3. Film Growth

Acheson grown, 6H-SiC single crystals were used as substrates. The crystals were diamond grown and polished to a I gm finish and then etched in HF (30 wt%) for 1 h prior to heating in vacuum (2 x 10-1 Pa) at 700 'C to remove any organic residue. The polyvinylmethylsilane precursor was dissolved in toluene to produce a 16 wt % solution with a viscosity of 1.3 MPa. A precursor film was formed on the substrate by dip-coating [10] by withdrawing after 1 min with a constant velocity of 2.7 cm/min. After drying, the adherent polymer, precursor film was pyrolyzed at 1100 'C in nitrogen (flow rate: 20 cm/min) in a tube furnace (Heraeus R0 4/25). Subsequent thermal treatments were performed in a graphite furnace (Gero HTO 2400/5) at 1600 °C for 10h in nitrogen. After each heat treatment, cross sectional TEM specimens were prepared as described elsewhere [111. All TEM studies were performed using a TEM 2000FX (JEOL) operated at 200kV and a Zeiss EM 912.

4. Results

Figure 2 shows a bright field TEM micrograph of the specimen heated at 1100 °C. As revealed by SAD (Selected Area Diffraction) a ≈ 200 nm thick amorphous SiC layer (α-SiC) has been grown on the 6H-SiC substrate. The roughness of the interface between the α-SiC layer and the 6H-SiC substrate is due to the initial surface roughness of the substrate produce during substrate preparation. A qualitative chemical analysis of the amorphous film by EELS showed that it contained C, Si and 0.

After heating the specimens at 1600 °C for 10 h, TEM revealed that the film was converted to an epitaxial β-SiC layer with a thickness of -200 nm as shown in Fig. 3. Figure 4 shows SAD results, revealing the following orientation relationship between film and substrate:



$$[011]\ \beta\text{-SiC} \parallel [2\bar{1}10]\ 6H\text{-SiC}$$
$$(\bar{1}\bar{1}1)\ \beta\text{-SiC} \parallel [0001]\ 6H\text{-SiC}.$$

Figure 3 also shows that the film contains a high concentration of defects at the β-SiC/6H-SiC interface and within the P-SIC film. The defects at the interface are due to substrate preparation, namely residual substrate roughness and dislocation arrays that extend from the surface into the substrate. Most of the defects in the P-SIC film are growth defects and may be caused by surface defects on the substrate as suggested by others [12,13,14]. The β-SiC film was investigated in the TEM with EELS indicating

that the film is composed mainly of Si and C.

5. Conclusions

A polyvinylmethylsilane precursor was successfully used to grow thin, single crystal SiC films on single crystal, 6H-SiC, substrates. Cross-section TEM revealed that the films grown at 1100 °C are amorphous and contained oxygen. At 1600 °C the precursor is converted to a single crystalline, β-SiC film and contained mainly Si and C. Defects were present within the single crystal film that may be caused by the roughness of the substrate.

Acknowledgments

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Table 1 Composition of the inorganic material derived from the polyvinylmethylsilane precursor after pyrolysis at 1100 °C in argon. [8]

elements:	C	Si	O
wt-%	47,4	50,0	1,4

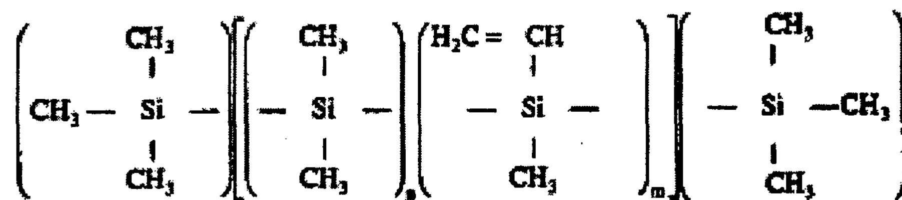

Fig. 1 Structure of polyvinylmethylsilane schematically. [8]

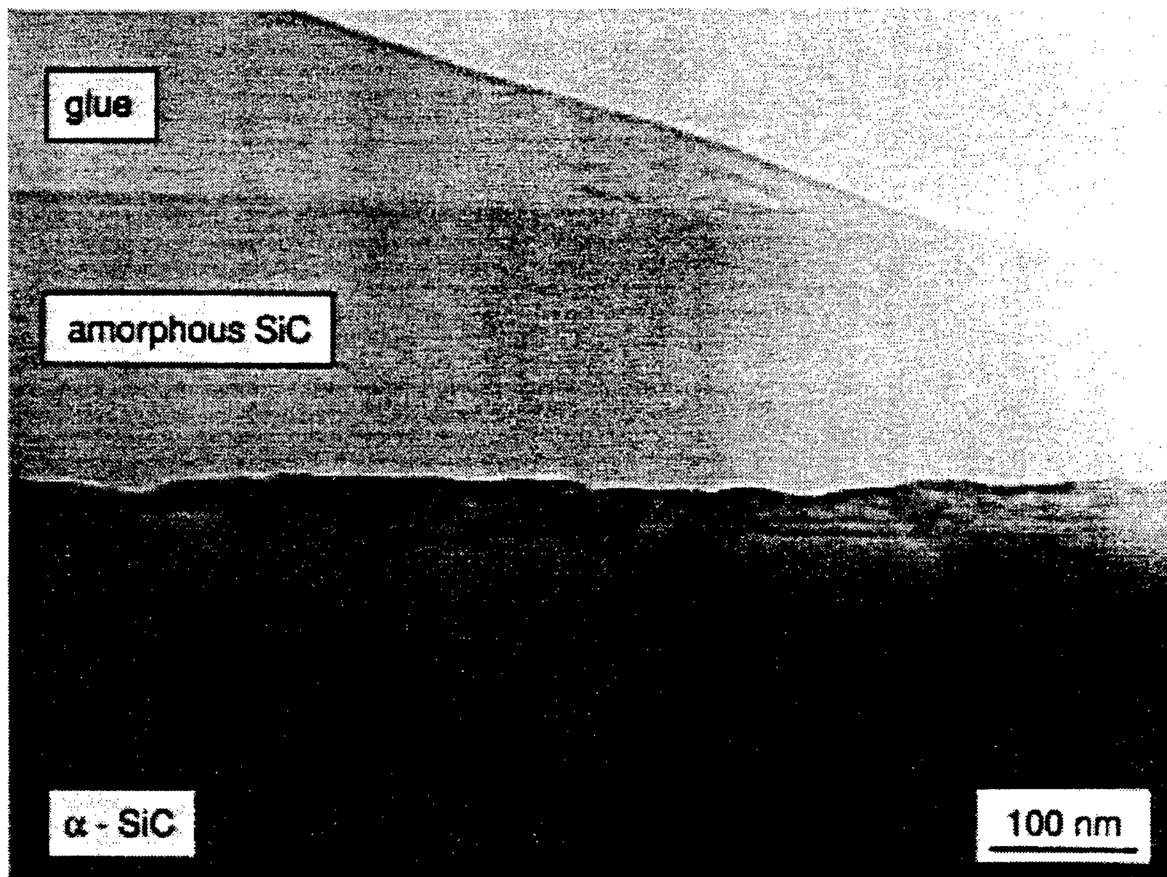

Fig. 2 Bright field TEM micrograph of the SiC film grown at 1100°C. The roughness of the interface between amourphous SiC film (a-SiC) and 6H-SiC substrate (α-SiC) is due to the initial substrate roughness.

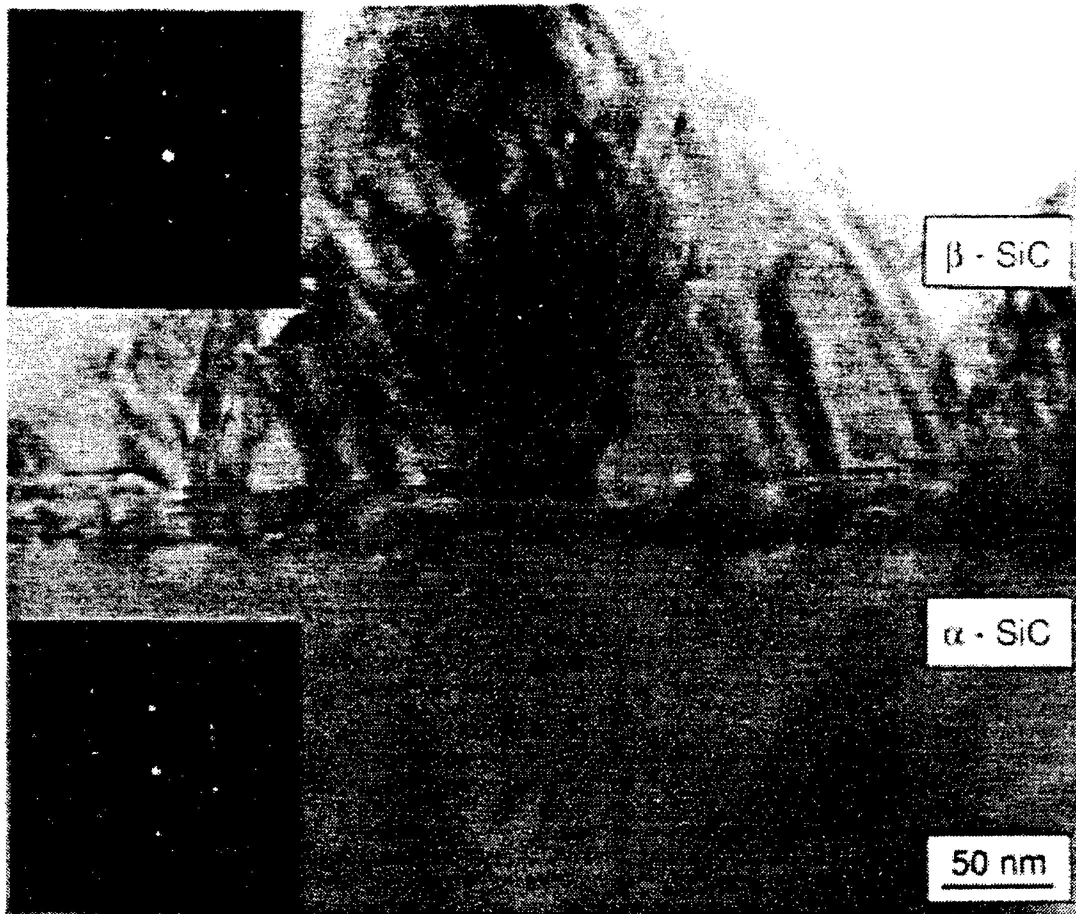

Fig. 3 Bright field TEM micrograph of the region around the 6H-SiC/β-SiC interface. SAD pattern of the film revealed that the film is single crystalline β-SiC (small diffraction pattern on the left side of the micrograph, electron beam along [011]β-SiC). A lot of defects are present in the β-SiC.

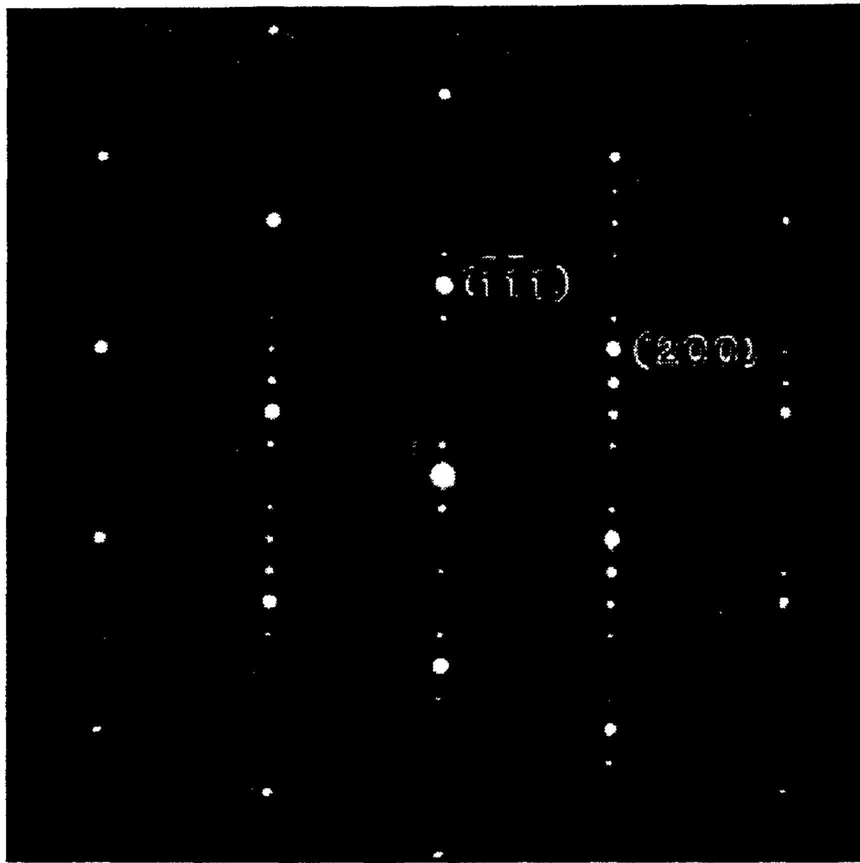

Fig. 4 SAD pattern of the β-SiC film and the 6H-SiC substrate (α-SiC) indicates that the film grows epitaxially on the substrate (reflections of the β-SiC are indexed, electron beam along [011]β-SiC).

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