Supersonic jet epitaxy of single crystalline cubic SiC thin films on Si substrates from t-Butyldimethylsilane

Jin-Hyo Boo 1, S.A. Ustin, W. Ho *

Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, NY 14853, USA

Received 8 May 1997; accepted 11 December 1997

Abstract

Cubic SiC thin films have been grown by supersonic jet epitaxy (SJE) using the single molecular precursor t-butyldimethylsilane (TBDMS), (CH₃)₃C-SiH(CH₃)₂. Single crystal cubic SiC thin films were grown on both carburized and uncarburized Si(100) at a temperature of 830°C. Highly oriented cubic SiC(111) thin films were obtained on carburized and uncarburized Si(111) substrates at 830°C. This growth temperature is much lower than conventional CVD growth temperatures. It is believed that this is the first report of SiC growth using t-butyldimethylsilane. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silicon carbide; Organometallic vapour deposition; Epitaxy; Silicon

1. Introduction

Cubic silicon carbide (3C–SiC or β-SiC) has attracted much interest due to its outstanding electrical, optical, and mechanical properties. Its high electron mobility (1000 cm²/V s) [1], high electron saturation velocity (calculated as 2–2.7 × 10⁷ cm/s at 2 × 10⁵ V/cm) [2], high breakdown electric field (5 × 10⁶ V/cm) [3], and high thermal conductivity (6.0 W/cm K) make it a promising semiconductor material for electronic devices operating under extreme conditions such as high power, high frequency, and high temperature [4–6]. Cubic SiC can also be used for optoelectronic devices which are blue or ultraviolet sensitive due to its wide band gap (2.3 eV) [7] and is considered a candidate for the emitter material in silicon heterojunction bipolar transistors (HBTs) [8]. Difficulties in growing large-area single crystal SiC have limited its development in these applications. The most common substrate material for cubic SiC epitaxy is silicon even though the large lattice mismatch (20%) introduces crystalline defects into the heteroepitaxial film (antiphase boundaries (APBs) on Si(100) and double positioning boundaries (DPBs) on Si(111) [9], reducing carrier mobilities and increasing junction leakage currents [10]. The high growth temperatures utilized for CVD (> 1200°C) further increase the problem due to the large thermal expansion mismatch (~ 8%) between Si and SiC. In addition, high growth temperatures can lead to unintentional autodoping, SiC precipitation, and alteration of previously incorporated dopant distributions. Lower temperature epitaxy is thus highly desirable from the point of view of device fabrication with heteroepitaxially grown cubic SiC on Si.

Most β-SiC growth proceeds through the use of separate precursors for silicon (SiH₄, Si₂H₆, SiH₂Cl₂) and carbon (C₂H₂, CH₄, C₃H₄). It had been proposed that SiC deposition temperatures can be lowered by using a single molecular precursor with preformed Si–C bonds. Recently, researchers have been successful in depositing β-SiC on silicon with a number of different organosilicon precursors including hexamethyldisilane [11–15], tetramethylsilane [16,17], methyltrichlorosilane [18–21], methylisilane [22–24], silacyclobutane [25,26], dimethylisopropylsilane [27], and bis-trimethylsilylmethane [28,29]. There are only a few reports, however, of single phase cubic SiC growth at temperatures below 1000°C [17,22–27]. The extra energy imparted to an organosilicon precursor molecule in a supersonic jet lowers the thermal energy, and thus the substrate temperature, necessary for the surface reaction to take place [28–32]. It is believed that SJE may be a viable technique for overcoming the detrimental effects of high temperature CVD.
2. Experimental

The growth apparatus consists of a two stage differentially pumped molecular beam line and a growth chamber (Fig. 1). Thin film growth was carried out in the stainless-steel UHV growth chamber (base pressure $1 \times 10^{-9}$ Torr) equipped with a quadrupole mass spectrometer (QMS) and an Auger electron spectroscopy (AES) system pumped by a LN$_2$ trapped diffusion pump. The beam line houses a long nozzle with a $150 \mu$m diameter orifice to supply acetylene ($C_2H_2$) for carburization. The substrate is located 45 cm from the nozzle orifice. A shorter nozzle with a $150 \mu$m diameter orifice is inserted directly into the growth chamber for high pressure growth with the organosilicon source. The substrate is located 4 cm from this nozzle orifice. Optical reflectivity, with a 10 mW He–Ne laser and a photodiode, is used for in situ, real-time monitoring of the film growth.

The substrates (2 cm × 2 cm) used in this study were p-type Si(111) and n-type Si(100). Substrates were cleaned ex situ by sequential immersion into baths of acetone, isopropyl alcohol, 48% HF solution, and deionized water, and then immediately loaded into the growth chamber. After the chamber achieved base pressure, the substrates were mild-annealed at 650°C for 1 h, annealed at 950°C for 15 min, and then brought to the deposition temperature. During the annealing process substrates were exposed to a supersonic jet of molecular hydrogen to minimize surface contamination. Sample temperature was monitored by a K-type thermocouple and an infrared pyrometer.

The commercially available (Gelest) single molecular precursor, t-butyldimethylsilane [(CH$_3$)$_3$C–SiH(CH$_3$)$_2$; TBDMS], a liquid at room temperature, was purified using freeze–pump–thaw cycles. The QMS was used to verify TBDMS entry into the growth chamber. The cracking pattern for the TBDMS molecule shows a series of peaks at 2, 15, 26, 45, 57, and 59 amu which correspond respectively to $H$, $CH_2$, $C_2H_2$, $CH_3–SiH_2$, $(CH_3)_2C^+$, and $(CH_3)_2–SiH^+$. Molecular hydrogen was bubbled through the TBDMS to transport it in vapor phase to the nozzle. Films were characterized in situ by AES and ex situ by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Standard $\theta$–$2\theta$ and rocking curve XRD was performed on a Scintag PAD-X diffractometer (CuK$\alpha$, $\lambda = 1.54$ Å). Azimuthal scans ($\varphi$-scans) were performed on a four circle diffractometer at the Cornell High Energy Synchrotron Source ($\lambda = 1.215$ Å). Film thickness was measured ex situ using ellipsometry and a surface profilometer (Alpha-step 200, Tencor Instruments). SiC films were grown on both carburized and uncarburized silicon surfaces. Carburization at 830°C by a supersonic beam of 4% acetylene seeded in hydrogen produced a 0.2 μm thick SiC layer. XRD was performed on the carburized silicon to verify single phase SiC formation. The chamber pressure during growth with TBDMS was about $1 \times 10^{-4}$ Torr. When SiC is grown with TBDMS on uncarburized Si, carburization may initially occur at the Si surface simultaneously with the growth of the SiC film. The X-ray diffraction patterns contain information from possibly SiC with different morphologies above the Si substrate.

3. Results and discussion

3.1. Si(111)

SiC was grown from TBDMS on both carburized and uncarburized Si(111) substrates at 830°C. Two sets of films were grown to test reproducibility. All film surfaces appear mirror-like, although films grown on the uncarburized surface appear to have a smoother surface morphology when viewed through an optical microscope. Films were grown to 0.7 μm thick at a growth rate of ~ 0.1 μm/h. Fig. 2 shows standard X-ray $\theta$–$2\theta$ diffraction
patterns for one set of epitaxial cubic SiC thin films grown on carburized (Fig. 2a) and uncarburized (Fig. 2b) Si(111). Both spectra show a single sharp peak at 35.6° corresponding to SiC(111) planes. The second set of films show similar spectra signifying all films are single phase. The FWHM of the SiC(111) 2θ peak for the film grown on the carburized surface (Fig. 2a) is 0.40°. For the film deposited directly on Si(111) (Fig. 2b) the FWHM of the SiC(111) 2θ peak is 0.35°. These results obtained with TBDMS at 830°C compare favorably with FWHM values reported by Yuan et al. for SiC films grown at 800°C with silacyclobutane on carburized Si(111) [25]. To test whether the films are truly single crystalline or highly 111 textured polycrystals, X-ray rocking curves (ω-scan) and azimuthal scans (φ-scan) were performed. Spreading in ω and φ is due to a combination of bending caused by the large thermal mismatch and mosaicity due to defects brought about by the 20% lattice mismatch. The insets in Fig. 2 show the rocking curves about the SiC(111) peaks. The rocking curve widths (Δω) for the four films lie between 2.7° and 3.4° with no noticeable improvement from carburization. The rocking curve widths are much larger than the 2θ widths implying that the film consists of a mosaic of microcrystals [33].

φ-scans were used to measure in-plane structural order. The diffractometer was set up to detect diffraction from the (220) family of planes as the SiC(111) film was rotated about its surface normal. As seen in Fig. 3 the periodicity of the peaks is 60°. Since the [111] axis in the zinc-blende structure is a 3-fold rotation axis, the φ-scan should show peaks every 120°. The 6-fold symmetry seen in Fig. 3 can be accounted for if two kinds of stacking sequences exist in the film, the ABCABC… and CBACBA… sequences. This leads to double positioning boundaries when islands of different stacking sequences coalesce. This type of defect has also been seen by Zhou et al. by TED [34] and by Wahab et al. by XRD [35]. The similarity in intensity of all the peaks indicates that neither sequence dominates. Carburization of the Si(111) surface did not seem to force preferential growth of one stacking sequence although it did reduce the peak widths. The carburization layer may help reduce the strain caused by the lattice mismatch between the SiC and the silicon substrate. It is unknown if the 6-fold symmetry exists within the carburized SiC layer itself. The breadth of the peaks is due to large variations in microcrystalline size and orientation. One growth was attempted with TBDMS on carburized Si(111) at 780°C without success. SiC formation at this temperature is likely limited by a low thermal reaction rate between the SiC surface and the TBDMS molecule.

3.2. Si(100)

Growth from TBDMS was also attempted on carburized and uncarburized Si(100) surfaces at 830°C. The film surfaces were smooth and crack-free when viewed under an optical microscope. Films were grown to 0.5 μm thick at a growth rate of ~ 0.07 μm/h, markedly slower than the growth on Si(111). Fig. 4 shows XRD spectra for these films. Only the SiC(200) peak at 41.4° appears in the diffraction patterns indicating epitaxial growth. The FWHM of the SiC(200) 2θ peaks are 0.62° on the carburized Si(100) (Fig. 4a) and 0.70° on the uncarburized Si(100).
Fig. 5. X-ray phi-scans detecting SiC 111 planes for cubic SiC 100 thin films grown at 830°C on (a) carburized Si(100), (b) uncarburized Si(100).

(Fig. 4b). These widths are noticeably higher than those measured for the SiC(111) peaks likely indicating a smaller average grain size [36]. Steckl et al. also saw wider 2θ widths for SiC(200) as opposed to SiC(111) when growing with silacyclobutane. The insets of Fig. 4 show the rocking curves for the films. The rocking curve peak widths for the films on the carburized and uncarburized Si(100) are 3.8° and 2.7°, respectively. φ-scans were also performed on these samples by detecting {111} peaks. Fig. 5 shows strong sharp peaks in the φ-scans for films on both surfaces. The four-fold symmetry of the peaks indicates that the films are single crystalline zinc-blende SiC(200). The φ-scan peak widths are much narrower for the SiC(200) films than for the SiC(111) films.

FTIR absorption measurements were done on all samples. Each film showed a strong absorption peak near 794 cm⁻¹ due to the Si–C stretching vibration in the SiC film. Lorentzian peak widths were similar for all films, ranging from 32 cm⁻¹ to 35 cm⁻¹.

4. Conclusion

SiC thin films have been grown for the first time using the single molecular precursor t-butyldimethylsilane. Epitaxy was initiated on four types of surfaces, carburized and uncarburized Si(111) and Si(100) at 830°C. This growth temperature is far below common CVD growth temperatures. Cubic single crystal films have been produced on Si(100) with a Δω as low as 2.7°. In-plane φ-scans show sharp four-fold symmetry. Highly oriented films were deposited on Si(111) with a Δω also as low as 2.7°. φ-scans show broad six-fold symmetry implying that two types of stacking sequences exist with equal probability within the SiC(111) films. Carburization of the Si(100) surface prior to deposition with TBDMS (at 830°C) did not seem to have any noticeable effect on film characteristics whereas growth on the carburized Si(111) surface showed a higher degree of in-plane order than growth directly on Si(111). Further study is necessary to understand the mechanism of dissociation and adsorption of the TBDMS molecule on silicon and silicon carbide surfaces.

Acknowledgements

Support of this research by the BMDO via the Office of Naval Research Grant Number N00014-93-0499, the STRR via the Office of Naval Research Contract No. N00014-95-C-0414, and the MRSEC Program of the National Science Foundation under Award No. DMR-9632275 is gratefully acknowledged. One of authors (J.-H.B) acknowledges the partial support from the Institute of Vacuum Industrial Technology in Sung Kyun Kwan University, Suwon, Korea. We would like to thank Dr. R.L. Headrick, Dr. S. Kycia, and Mr. C.P. Long for assistance in X-ray φ-scan measurements.

References


