Structural characterization of nanometer SiC films grown on Si

J. P. Li and A. J. Steckl
Nanoelectronics Laboratory, Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0030

I. Golecki and F. Reidinger
Allied-Signal Inc., Morristown, New Jersey 07962-1021

L. Wang, X. J. Ning, and P. Pirouz
Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106

(Received 24 November 1992; accepted for publication 25 March 1993)

Continuous, ultrathin silicon carbide (SiC) films of less than 10 nm have been grown on Si by rapid thermal chemical vapor deposition carbonization with high propane flow rates at 1100–1300 °C. X-ray and electron diffraction techniques indicated a monocrystalline structure for these nanometer-scale films. High-resolution transmission electron microscopy reveals that five SiC planes are aligned with four Si planes at the SiC/Si interface. The Fourier transform infrared spectrum of the SiC films exhibits the characteristic Si-C absorption peak at around 800 cm^{-1}, with a FWHM of 45 cm^{-1}.

Due to its large energy band gap and other promising semiconductor properties, silicon carbide (SiC) has potential for high performance as a wide band-gap emitter to the SiC/Si heterojunction bipolar transistors. Relatively thin SiC can be formed by the process of carbonization in which the Si surface is exposed to a C-containing precursor at high temperature and is converted into SiC. Thicker SiC films can be subsequently formed on this carbonized layer, if desired, by the addition of Si-containing precursor into the gas stream. SiC growth by carbonization is intrinsically selective on Si with SiO_2 serving as an excellent mask. This enables a relatively simple and direct incorporation of carbonization into a conventional Si fabrication process. However, the SiC films grown on Si have been traditionally plagued with the concurrent formation of voids in the Si substrate underneath the film.[1,2] It has been shown by the authors that void-free SiC films could be formed on Si under certain growth conditions[3] involving high precursor flow rate. The SiC films formed under these conditions are self-limiting in thickness, e.g., reaching only about 10 nm after 90 s at a reaction temperature of 1300 °C. SiC/Si heterojunction diodes fabricated using these nanometer-thin films have shown very good forward current-voltage characteristics with a 1.2 ideality factor.[4] It is, therefore, of great importance to characterize these ultrathin SiC films and to understand the initial nucleation and growth process. The materials characterization is made particularly difficult by the very small volume of material which can be conveniently analyzed.

The SiC-on-Si thin films were grown at the University of Cincinnati by the rapid thermal chemical vapor deposition (RTCVD) technique. Detailed information on the SiC growth process and the RTCVD system can be found in Ref. 3. Briefly, in the RTCVD technique rapid heating and cooling of the sample take place under conditions of continuous gas flow of appropriate precursors. The sample temperature, therefore, essentially acts as a growth switch. The SiC films discussed here were formed at atmospheric pressure by a two-step process: *in situ* cleaning followed by carbonization. Prior to being loaded in the RTCVD system, the Si substrates were dipped in diluted HF, rinsed in de-ionized H_2O, and blown dry by N_2. *In situ* cleaning was carried out at atmospheric pressure in HCl/H_2 at 1200 °C for 2 min. Carbonization was performed at 1300 °C for 90 s with a temperature ramp rate of 50 °C/s, a C_3H_8 (5% diluted in H_2) flow rate of 29 sccm, and an additional 0.9 lpm of H_2 carrier gas. These growth conditions result in SiC films with thickness of about 10 nm.

The film thickness and crystallinity of SiC formed by carbonization was found to be strongly dependent on the C-bearing gas concentration in the gas stream.[3] In the case of the propane precursor in our RTCVD chamber, the SiC film thickness exhibits a maximum at the so-called transition propane flow rate of 7–10 sccm, for a carrier gas flow rate of 0.9 lpm. At the transition flow rate the SiC films are monocrystalline and their thicknesses increase linearly with reaction time. At flow rates below the transition rate, the films are polycrystalline with a dendritic structure. The region of interest here is that of void-free growth which occurs at flow rates significantly higher (20–50 sccm) than the transition rate. At these flow rates the SiC films are uniform and smooth but extremely thin, usually less than 10 nm. These films are difficult to analyze with conventional analytical equipment. The composition-depth profile of an ultrathin film grown with 30 sccm propane flow rate was obtained by a careful use of Auger electron spectroscopy (AES). The AES profile exhibited[5] an uncorrected Si:C ratio of ~55:45, which is similar to SiC thick films and standard crystals.

To investigate the crystal structure of these films, as well as the interface between the Si substrate and the SiC film, we have utilized high-resolution transmission electron microscopy (HRTEM) and diffraction (TED). Cross-sectional SiC/Si samples were prepared and analyzed at the Case Western Reserve University using the 400 keV JEOL 4000EX TEM system. A HRTEM microphoto-

Downloaded 07 Oct 2003 to 129.137.210.120. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

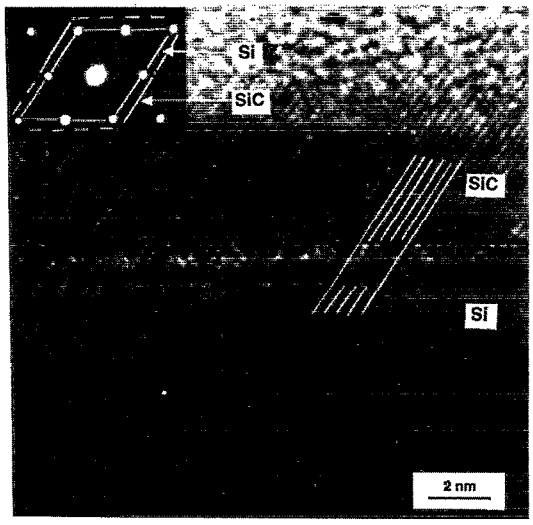

FIG. 1. HRTEM microphotograph of 8 nm SiC film grown by RTCVD at high propane flow rate. Inset: TED pattern of region including both SiC film and Si substrate.

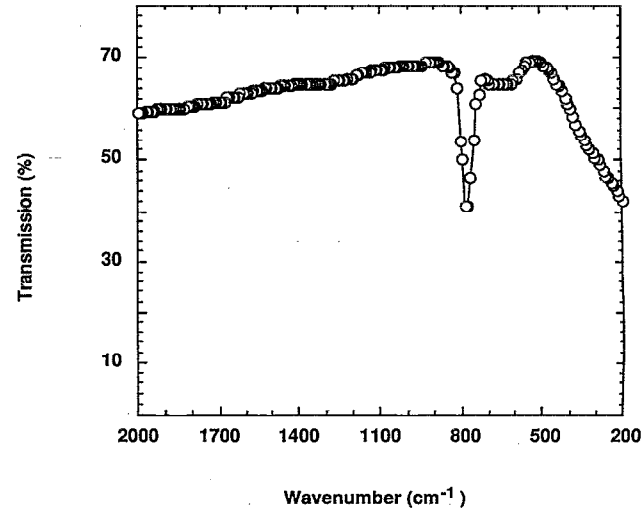

FIG. 3. FTIR spectrum of 8 nm SiC film.

graph of a ~8 nm SiC film on Si grown by RTCVD at high C_3H_8 flow rate is shown in Fig. 1. The SiC {111} lattice planes are generally well aligned with those of the Si substrate. However, only every fourth Si plane appears to actually align with every fifth SiC plane. This corresponds to the ratio of bulk lattice constants between Si and SiC, namely 5.431 Å/4.359 Å. The irregularly shaped band at the SiC/Si interface is thought to be an artifact introduced by uneven SiC and Si milling rates during the ion thinning process. The TED pattern shown in the inset of Fig. 1, which was taken over a much large sample area, indicates good crystallinity of the SiC film and the alignment of the film with the Si substrate.

X-ray diffraction (XRD) of the SiC ultrathin films was carried out at Allied-Signal by means of a 12 kW rotating anode Rigaku spectrometer in order to provide sufficient signal-to-noise ratio for the measurements. The XRD spectrum of the same 8-nm SiC film is shown in Fig. 2. A single distinct peak appears at $2\theta=41.4°$, which is identified as the (200) SiC reflection, with no other peaks appearing over the scan range from 30° and 45°, indicating crystallinity of the SiC film.

Fourier transform infrared (FTIR) spectroscopy was utilized at Allied-Signal to determine the atomic bonding in the ultrathin SiC films. A Perkin–Elmer Model 1600 transmission FTIR system was employed for the analysis. A FTIR transmission spectrum of the 8-nm SiC film is shown in Fig. 3. The spectrum displays only the characteristic Si—C bond absorption peak at ~800 cm^{-1}. The FWHM of the peak is 45 cm^{-1} which is similar to that of thick monocrystalline SiC film grown on Si (~30 cm^{-1}).

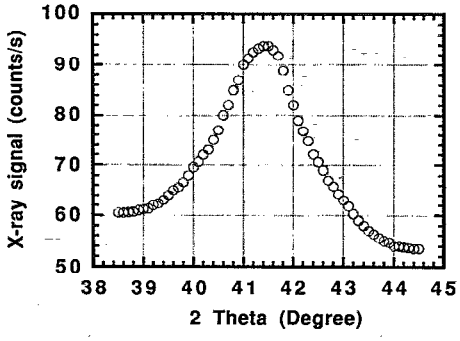

FIG. 2. XRD spectrum (data smoothed for clarity) of 8 nm SiC film.

It has been previously suggested[6] that the SiC "buffer" layer formed by carbonization prior to SiC growth accommodates the large lattice mismatch between the two materials by gradually changing its composition from SiC to Si. The present evidence supports the theory[7] that the buffer layer is not compositionally and structurally graded. Instead, it appears that the buffer layer immediately takes the unstrained SiC structure which is aligned, but not epitaxial, to the Si substrate. The lattice mismatch produces a misfit dislocation at every fifth SiC plane. This 5:4 SiC-to-Si lattice plane match was first reported by Ernst and Pirouz[8] for selected (away from voids) regions of a SiC buffer layer grown with conventional propane flow rate conditions. Our results indicate that this 5:4 match is extended over the length of the entire layer when void-free film growth conditions are employed.

In a pioneering paper,[9] Mogab and Leamy developed the basic model for SiC carbonization growth on Si including the critical element of preferential outdiffusion of Si through pores in the film to reaction sites. They also observed that as the hydrocarbon partial pressure increases beyond a certain value, the pores in the SiC film are sealed, and further growth is effectively stopped. In this situation, Mogab and Leamy assumed that the high population of initial SiC nuclei are randomly oriented, inevitably resulting in a polycrystalline film. No data were given to support this assumption. Our results agree with those of Mogab and Leamy as far as the surface sealing aspect of the process at high hydrocarbon pressure is concerned. However, our TEM and diffraction analyses of these ultrathin SiC layers indicate that a monocrystalline structure is obtained,

Downloaded 07 Oct 2003 to 129.137.210.120. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp

implying that coordination exists between the initial SiC nuclei.

Two of the authors (J.P.L. and A.J.S.) gratefully acknowledge the support of this work at University of Cincinnati by the Ohio Edison Materials Technology Center.

[1] J. A. Powell, L. G. Matus, and M. Kuczmarski, J. Electrochem. Soc. **134**, 1559 (1987).
[2] P. Liaw and R. F. Davis, J. Electrochem. Soc. **132**, 642 (1985).
[3] A. J. Steckl and J. P. Li, IEEE Trans. Electron Devices **ED-39**, 64 (1992).
[4] P. H. Yih, J. P. Li, and A. J. Steckl (unpublished).
[5] A. J. Steckl and J. P. Li, Thin Solid Films **216**, 149 (1992).
[6] S. Nishino, H. Suhara, H. Ono, and H. Matsunami, J. Appl. Phys. **61**, 4889 (1987).
[7] P. Pirouz, *Mechanisms of Epitaxial Growth of Polar Semiconductors on (001) Silicon* (Springer, New York, 1989), Vol. 35, p. 200.
[8] F. Ernst and P. Pirouz, J. Mater. Res. **4**, 834 (1989).
[9] C. J. Mogab and H. J. Leamy, J. Appl. Phys. **45**, 1075 (1974).

Downloaded 07 Oct 2003 to 129.137.210.120. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/aplo/aplcr.jsp