Characterization of 3C–SiC crystals grown by thermal decomposition of methyltrichlorosilane

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(Received 30 July 1996; accepted for publication 20 August 1996)

Single crystal 3C–SiC platelets, formed by thermal decomposition of methyltrichlorosilane at 1650–1750 °C, have been characterized in terms of structure and morphology. The platelets are ~3–5 mm in length and 1–1.5 mm in thickness. The (111) C face of the crystal, which has an effective zero growth rate, presents a large, mirrorlike surface in the as-grown 3C crystals. Atomic force microscopy indicates that these *as-grown* surfaces are extraordinarily flat and uniform, with a mean surface roughness of 1–2 Å. This value is comparable with the roughness of state-of-art *polished* Si wafers. X-ray rocking curves of the ⟨111⟩ peak were obtained with a linewidth of 12.3 arcsec. This is the smallest value reported to date for any polytype of SiC. Raman spectroscopy at 300 K reveals a very sharp TO–phonon peak at 797.8 cm^{-1}, with a linewidth of 2.1 cm^{-1}. © *1996 American Institute of Physics.* [S0003-6951(96)00651-1]

Silicon carbide is a wide band-gap semiconductor under active development for high power, temperature, and frequency device applications. Several review articles cover various aspects of these developments, for example by Morkoç *et al.*[1] and by Edgar.[2] SiC crystals exhibit many structures depending on the stacking sequence of Si–C tetrahedra. The SiC polytypes that have been explored the most have either the zinc-blende (3C) or the hexagonal (4H or 6H) structures. While 3C has the highest electron mobility (~1000 cm^2/V s) of all SiC polytypes, interest has concentrated on the hexagonal polytypes because of the commercial availability of substrates cut from bulk crystals grown by a modified sublimation technique.[3,4] Due to the general unavailability of bulk 3C–SiC crystals, most recent work on 3C used thin film growth on Si substrates (for a review see Davis *et al.*[5]). 3C–SiC-on-Si growth was made possible by the introduction[6] of a buffer layer that partially accommodated the large lattice mismatch. However, recently there has been renewed interest in the bulk growth of 3C–SiC by the sublimation technique using seeds consisting of 3C–SiC films grown on (and removed from) Si,[7] and 6H–SiC crystals.[8,9] In this context, it is useful to be aware of the capabilities of previously developed vapor phase bulk crystal growth techniques for the 3C polytype. Most of the reports[10–13] of vapor phase 3C crystal growth utilized the pyrolytic decomposition of chlorine-containing organosilanes in conjunction with heated graphite rods or tubes as susceptors.

In this letter, we report several newly characterized aspects of vapor phase grown 3C–SiC crystals, including atomic force microscopy (AFM) of the as-grown crystal surfaces, multiple-crystal x-ray diffraction (MCXRD), and Raman spectroscopy. Single crystal 3C–SiC platelets have been grown[14,15] from the thermal decomposition of methyltrichlorosilane (MTCS–CH_3SiCl_3) at the Baikov Institute. MTCS is a colorless liquid at room temperature (with a boiling point of 66 °C). No metallic parts were used in the reactor because MTCS produces HCl in contact with moisture. The SiC growth is carried out in a high flow of H_2 on a resistively heated graphite rod at temperatures ranging from 1650 to 1750 °C. This technique has yielded some of the purest and largest 3C–SiC crystals to date: ~3–5 mm in length and 1–1.5 mm in thickness. Undoped crystals appear yellow under normal light, while *n*-type (N-doped) crystals are dark green and *p*-type (Al- and B-doped) crystals are black.

An example of an undoped 3C–SiC crystal grown by MTCS pyrolysis is the platelet-shaped crystal with 5.3 mm in length and ~1 mm thickness shown in Fig. 1. The top surface, shown in the photograph of Fig. 1(a), is the (111) C face of the crystal, which has an effective zero growth rate compared to the other growth planes. This surface is not processed after crystal growth and presents a remarkably flat- and mirror-finished plane. The back side of the crystal consists of a smaller (111) Si face bounded by inclined (111) planes.

X-ray diffraction (XRD) rocking curve ($\omega/2\theta$) measurements have been performed using the Philips Xpert system. The monochromator of this system consists of four channel-cut Ge crystals oriented along the (220) plane. In this configuration, a maximum resolution of ~11 arcsec can be achieved using a Si (111) wafer. An XRD rocking curve of the ⟨111⟩ peak of the 3C crystal shown in Fig. 1 is presented in Fig. 2. The full width at half-maximum (FWHM) of the

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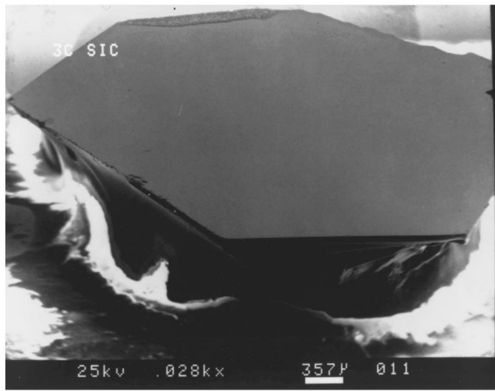

FIG. 1. Photograph of undoped 3C–SiC crystal grown by methyltrichlorosilane.

3C–SiC ⟨111⟩ line is approximately 12.3 arcsec. For comparison, commercially available 6H–SiC measured on the same system exhibits multiple overlapping peaks with the FWHM of the largest peak being ~70 arcsec. Conventional XRD scans ($\theta/2\theta$) of the crystal reveal only the ⟨111⟩ and ⟨222⟩ reflections of the 3C polytype over the dynamic range (10^5) of the measurement.

One of the most interesting aspects of the growth by this technique is the presence of a large, mirrorlike surface in the as-grown 3C crystals. Using AFM (Digital Instruments Dimension 3000) in the tapping mode we have determined that these as-grown surfaces are extraordinarily flat and uniform. This value is comparable with the roughness of state-of-art polished Si wafers. An AFM image of a 1×1 μm^2 area of this surface is shown in Fig. 3. Several dust particles show up as large and bright (and, therefore, relatively tall) white features in the image. Excluding these larger particles, which are unrelated to the crystal growth, a mean surface roughness (R_a) of 1.46 Å is obtained over the surface contained within the inner black rectangle. Additional information regarding the surface contained within the black rectangle is given in the *box statistics* shown in Fig. 3. Similar information for the entire surface is given in the *image statistics* in Fig. 3. It is interesting to point out that, even when one includes the large particles in the calculation of the surface roughness, the R_a over the entire image is still only 1.72 Å.

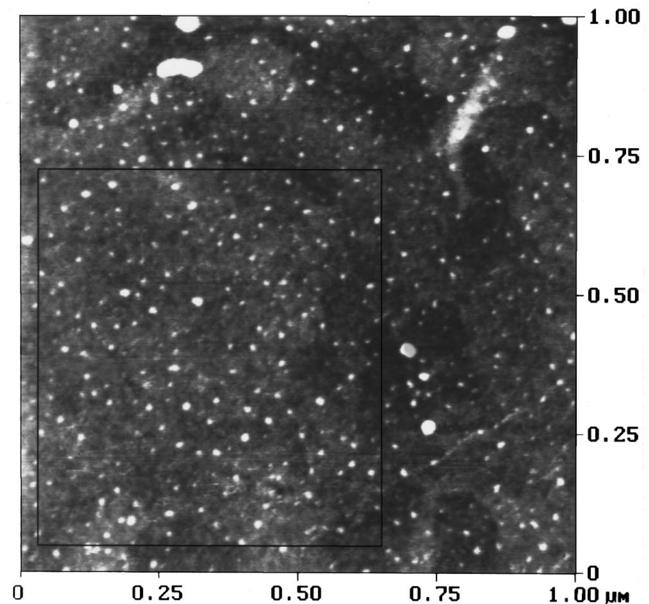

Image Statistics

Img. Z range	5.841 nm
Img. Rms (Rq)	0.267 nm
Img. Ra	0.172 nm
Img. Srf. area	1.002
Img. Srf. area diff	0.244 %

Box Statistics

Z range	2.386 nm
Rms (Rq)	0.201 nm
Mean roughness (Ra)	0.146 nm
Surface area	0.421
Surface area diff	0.224 %

FIG. 3. Atomic force microscopic image of the (111) C face of 3C (upper figure) and surface roughness analysis (lower table).

Micro-Raman spectroscopy with spatial resolution of 1–2 μm was performed in the backscattering mode using Ar^+ laser excitation with a wavelength of 514.5 nm. Figure 4 shows a Raman spectrum obtained at room temperature from the (111) surface of the 3C–SiC crystal obtained using 5 mW of power and a 50× objective. Two sharp lines are observed at 797.8 cm^{-1} (TO phonon) and 972.8 cm^{-1} (LO

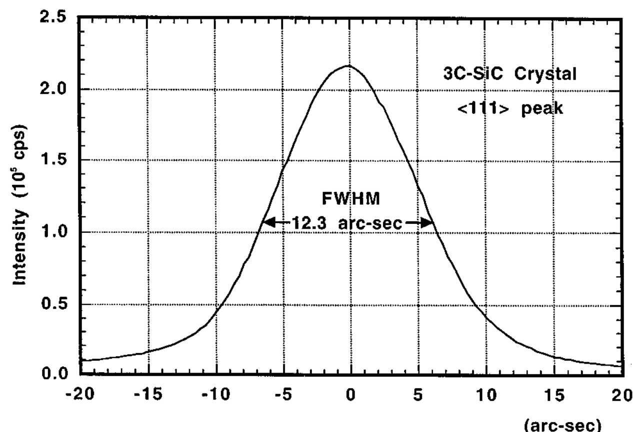

FIG. 2. Rocking curve x-ray diffraction spectrum of 3C–SiC crystal.

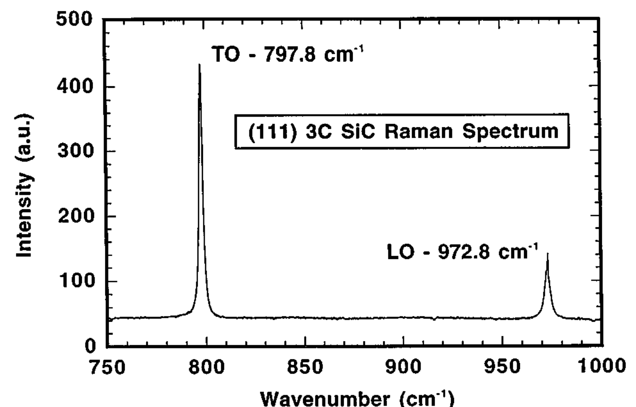

FIG. 4. Raman spectrum taken in the backscattering configuration from the (111) surface of 3C–SiC crystal at 300 K.

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phonon). Spectra obtained from six different locations provided an average FWHM for the TO and LO lines of ~2.1 and ~3.5 cm^{-1}, respectively. These values are not corrected for the 1–2 cm^{-1} resolution of Jobin– Yvon U-100 double monochromator operated with 200 μm slits. For comparison purposes, we have measured the Raman peak of a Si wafer at 521 cm^{-1} under the same conditions and obtained a FWHM of ~2.5 cm^{-1}. For relatively thick (5 and 12.7 μm) 3C–SiC films grown on Si (100) substrates, where only the LO phonon is allowed by the Raman selection rules, LO–phonon lines have been reported with line widths (FWHM) of ~5 cm^{-1} (Ref. 16) and 7 cm^{-1} (Ref. 17), respectively.

In summary, we have reported the structural characteristics of 3C crystals grown by methyltrichlorosilane. The crystals exhibit remarkable properties as exemplified by instrument-limited XRD and Raman spectroscopy results. The uniquely flat and smooth (111) C surface can be used for fabricating exploratory 3C–SiC devices, even though currently the crystal size is fairly small. We conclude that an investigation pursuing potential improvements in the vapor phase growth of 3C–SiC leading to crystals with larger dimensions would be desirable at this time.

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