

## Internal Atomic Distortion and Layer Roughness of Epitaxial SiC Thin Films Studied by Short Wavelength X-Ray Diffraction

G. Xu

*Department of Materials Science, National University of Singapore, Singapore 119260  
and Department of Materials Science and Engineering, McMaster University, Hamilton, L8S 4L7, Canada*

Z. C. Feng

*Institute of Materials Research & Engineering, 3 Research Link, 117602 Singapore  
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Epitaxial silicon carbide thin films grown on a silicon substrate were examined by short wavelength (0.71 Å from a molybdenum anode) x-ray diffraction to study their atomic distortion and internal layer roughness. Up to 5 order Bragg peaks along (100) were measured and crystallographic structure factors were obtained. Electron density distributions along the surface normal were reconstructed via Fourier transform. In comparing to the ideal situation, it was found that, due to the lattice mismatch, the silicon atoms are no longer fixed on the same atomic plane, thus the corresponding electron distribution maxima were broadened. Also, the maxima for carbon atoms are flattened, indicating the randomized locations.

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Silicon carbide with over 250 polytypes is a promising material system for modern electronic and optoelectronic devices working in high temperature, high power, high frequency, and harsh environments [1–3]. It possesses many unique properties, such as wide band gap, high electric breakdown strength, high thermal conductivity, and excellent thermal and chemical stability. Research on SiC has attracted attention in the early stage of Si development [1]. However, due to the lack of proper growth technology for the large size of wafers, development on SiC was hindered while technology development on Si has advanced to a high degree. Interest in SiC has been renewed since the 1980s because of two major technology breakthroughs. One is the successful growth of epitaxial cubic (3C-) SiC film on Si substrate by way of chemical vapor deposition [4]. The other is the development of the modified sublimation method for growing a large boule of bulk SiC single crystals [5], which is based upon a Lily technology developed in 1955 [6]. In the 1990s, large sizes of 6H and 4H SiC wafers have been commercially available, which has greatly promoted research and development on SiC and applications [7]. For the device applications, heterogeneous epitaxial 3C-SiC thin film, grown on top of single crystal silicon and homoepitaxial SiC on SiC (6H on 6H and 4H on 4H) substrate by chemical vapor deposition (CVD) are the most popular [1,2,4,7].

To characterize the thin films, x-ray diffraction (XRD) is commonly used to measure the lattice constant from the Bragg peak position, and the crystal quality through the Bragg peak profile. In the research and development activities on SiC materials and devices in recent years, XRD has been widely used to characterize the crystalline quality of cubic SiC on Si(100) [8,9] and on Si(111) [10]. It can also be used to study ion implantation in SiC [11,12],

to investigate polymorphism [13,14], to monitor the alteration of polytypes during growth [15], to evaluate the recrystallization and the orientation relationship [16], and to explore heavily doping [17] and doping induced mismatch through reciprocal maps [18].

Traditionally, most of the XRD studies on SiC materials [5–18] employed the copper source with 1.54 Å radiation. The analyses of XRD patterns on the diffraction peak position, intensity, and width can lead to information on sample structure, crystallinity, perfection, defects, strain, etc. XRD line widths are related to the size (depth) and the mosaicity of the coherent region. Recently, the synchrotron radiation section topography has been also applied to investigate the growth process and sample quality of SiC crystals [19].

Usually no information from inside the unit cell, such as the internal atomic layer arrangement, can be extracted from the XRD investigation of SiC. Because of the lattice mismatch, for example for the case of 3C-SiC grown on Si, the internal Si and C atomic layers near the interface region might be distorted or have a complicated arrangement, as shown in Fig. 1. Up to now, there are no details studied in these internal atomic layer arrangements.

Using short wavelength x-ray, a new method is presented here, to retrieve the atomic internal layer distortion or roughness. It employs a molybdenum anode to generate a wavelength of 0.71 Å, less than one-half of that from a copper anode. This allows us to measure the Bragg reflections up to the 5th order, along the normal of the thin films of either (100) or (111) orientation. That is compared with the availability of only 2 orders of Bragg peaks from a common copper anode with a radiation wavelength of ~1.54 Å only. From the *peak intensities*, the absolute values of the crystallographic structure factors,  $|F(hkl)|$ , can then be deduced, after which the electron density of the

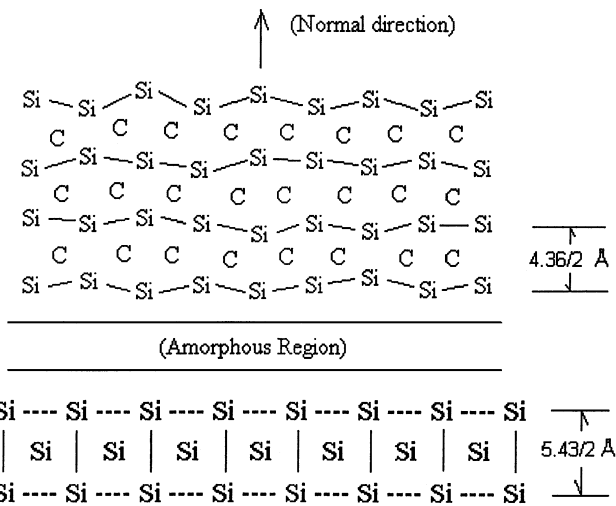


FIG. 1. The cross-sectional view of 3C-SiC on single crystal silicon.

thin film crystal can be recovered using Fourier transform, via,

$$\rho(x, y, z) = \sum_{hkl} |F(hkl)| \times \cos(2\pi[hx/a + ky/b + lz/c] - \phi_{hkl}), \quad (1)$$

where  $a, b, c$  are the lattice constants along  $x, y, z$ , and  $\phi_{hkl}$  is the phase [20]. They are compared with the calculated electron distribution using documented atomic scattering factors. The atomic layer roughness can therefore be quantified from the broadening (flattening) of the electron distribution maxima for silicon and carbon atoms.

Experimental SiC thin films, including 3C-SiC grown on Si(100) and 6H-SiC grown on 6H-SiC, are involved. Two 3C-SiC/Si with the film thickness of  $\sim 6 \mu\text{m}$  for sample 1 (grown for 2 h) and  $\sim 12 \mu\text{m}$  for sample 2 (grown for 4 h), and one 6H-SiC film with a thickness of  $\sim 6 \mu\text{m}$  homoepitaxial on 6H-SiC substrate were studied. Short-wavelength x rays were obtained from a Siemens D8 diffractometer using a molybdenum anode ( $K\alpha 1$  only). The intensity data were collected by a scan of  $0.004^\circ$  per  $2\theta$  step.

In a usual diffractometer, due to simple collimation and a broad spectrum ( $K\alpha 1 + K\alpha 2$ ) in the incident beam, an intensity maximum contains simultaneous diffraction contributions from a large volume surrounding a reciprocal lattice point. Thus, this maximum is not equal to the Bragg peak intensity, contributed only by the center of this volume [20]. A sample has to be scanned continuously, to 1st measure the integrated intensity over a range of  $2\theta$  (e.g.,  $0.5^\circ$ ). Assuming a standard peak profile, one can then calculate the peak intensity from the integrated intensity. The Lorentz factor must be used in the calculation, to compensate for the changing sweeping time of various reciprocal lattice points through the Ewald sphere

[20]. However, such a scheme is not applicable because of the lattice distortion, which changes the standard peak profile. Therefore, here we have to use a highly collimated and monochromatic beam ( $K\alpha 1$  only), to ensure that only a tiny volume surrounding a reciprocal lattice point is covered at any time moment. (The  $2\theta$  resolution is  $< 0.002^\circ$ , which is much less than the Bragg peak width.) With the step mode, we are able to measure the intensity variation near the reciprocal lattice point. The peak intensity can then be directly obtained by the intensity maximum without involving the Lorentz factor.

In fact, what we are measuring here are the peak intensities varied by the mosaic spreading along the transverse direction, which are directly related to the variation of lattice constants of the blocks projected onto the film normal (the scattering vector).

Using molybdenum anode, the peak intensities from  $\omega$ - $2\theta$  scan along the surface normal of a 3C-SiC/Si thin film sample (growth time = 2 h), are plotted in Fig. 2, where up to 5 Bragg peaks due to SiC(200, 400, ..., 1000) are presented along  $2\theta = 18.7\text{--}109^\circ$ . Peaks due to the silicon substrate are excluded, although they are detectable. Instead of the detailed peak profile, from which the peak breadth is usually studied, we focus on the peak intensity of various Bragg reflections, in order to use Eq. (1) to investigate the atomic arrangement within the crystalline unit cell along the normal direction. It is known that the Bragg peak intensities are proportional to the square of the structure factors  $|F(hkl)|^2$ , after being corrected by the polarization factor and Debye factor for thermal vibration (because the scan was done by step mode rather than continuous mode, no Lorentz factor is involved):

$$I(hkl) \propto (1 + \cos^2 2\theta)/2 \exp(-2M) |F(hkl)|^2, \quad (2)$$

where  $M = B(\sin\theta/\lambda)^2$ , and  $B$  is the thermal Debye parameter measuring the thermal motion [21]. Using  $B = 0.25$  as the average for silicon and carbon,  $|F(200\text{--}1000)|$  for sample 1 were obtained from Eq. (2) to be 9.63, 8.6,

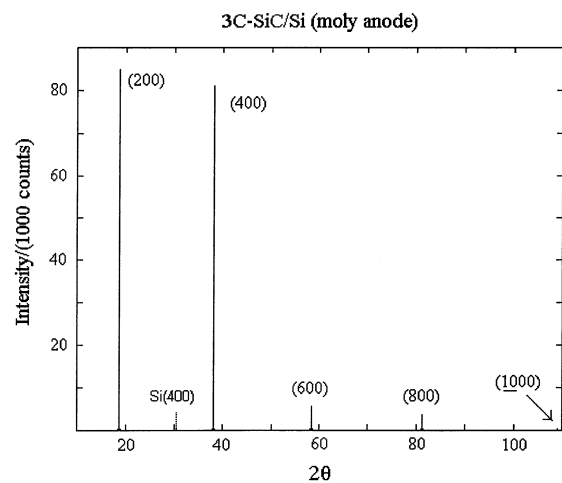


FIG. 2. The first 5 Bragg peak intensities of 3C-SiC.

TABLE I. A Comparison of the theoretical and experimental structure factors (normalized) for 3C-SiC.

	$F(200)$	$F(400)$	$F(600)$	$F(800)$	$F(1000)$
Experimental 3C-SiC film (6 $\mu\text{m}$ )	9.54	8.53	2.32	2.01	0.59
Experimental 3C-SiC film (12 $\mu\text{m}$ )	8.38	8.85	2.67	2.41	0.69
Theoretical values of 3C-SiC	5.83	8.49	3.05	4.40	1.19

2.34, 2.03, and 0.60. Similarly, the structure factors for sample 2 were 9.47, 10.0, 3.02, 2.73, and 0.78 (in arbitrary units).

To use these  $F(hkl)$  to reconstruct the atomic arrangement via Fourier transform using Eq. (1), we compare the measured structure factors with the calculated ones for the ideal situation, i.e., when the silicon atoms are sitting on 0, 1/2, and 1, and the carbon atoms are in 1/4 and 3/4 of the relative coordinates of the unit cell. In this case, the internal atomic layer arrangement is not distorted, and there is no internal atomic layer roughness involved. We have

$$\begin{aligned}
 F(h00) &= \sum_j f_j(\sin\theta/\lambda) \exp(2\pi i h x_j/a) \\
 &= f_{\text{Si}}(\sin\theta/\lambda) + f_{\text{C}}(\sin\theta/\lambda) \exp(2\pi i h/4),
 \end{aligned}
 \tag{3}$$

where the last step is valid only for  $h = \text{even numbers}$ . Note  $f_{\text{Si}}(\sin\theta/\lambda)$  and  $f_{\text{C}}(\sin\theta/\lambda)$ , the atomic scattering factors for silicon and carbon atoms, respectively, are dependent on the scattering angle and can be obtained from Ref. [21]. The resulting values are 5.83, 8.49, 3.05, 4.40, and 1.19 for  $F(200, 400, \dots, 1000)$  (all  $\phi_{h00}$  are zero), respectively.

Following Eq. (1), the 1D electron densities along the film normal can now be constructed using Fourier transform. Because of the arbitrary proportional constant in Eq. (2), to compare the calculated and measured results, these structure factors were “normalized” by a constant, so that the total area under each electron distribution curve is the same. However, in the present case the measured and calculated  $F(h00)$  numbers happen to be very close, such that the normalization factors all fall in between 1.0–1.15. The resulting numbers and the theoretical values are listed together in Table I. It is obvious that the numbers are in descending order, with the thinner film being the fastest when going from 200 to 1000.

From the resulting plot (Fig. 3), it is clear that the Si peak is wider for both heteroepitaxial SiC thin films. This indicates that there is indeed roughening of the Si plane within the silicon-carbide layers, although there is an amorphous region in between the thin film and the substrate silicon (Fig. 1). The amount of distortion or roughness of the Si planes inside the epitaxial SiC film can be estimated by the increase of the full width at half maximum (FWHM) of the Si maxima from that of the ideal case. For

example, the FWHM of sample 1 (6  $\mu\text{m}$ ), is found to be 41% larger than that of the theoretical value. Similarly, the FWHM of sample 2 (12  $\mu\text{m}$ ) is about 29% larger. Comparing these numbers against the film thickness, one can conclude that the distortion of atomic layers or the internal roughness of the individual atomic plane must be less serious for the layers far away from the substrate. Therefore, the averaged internal roughness, which is shown by the x-ray diffraction, becomes smaller when the films are thicker.

Moreover, it is interesting to observe from Fig. 3 that within the epitaxial thin film, the electron density for carbon is decreased, with no appreciable increase of the FWHM. This can happen only when some of the carbon atoms are relocated far away from their original positions. This is not unexpected under the high degree of roughness and distortion for the silicon atoms. In addition, the influence of the cutoff at (1000) for the Fourier series in Eq. (1) must be small, since the  $\frac{1}{8}$ th maxima predicted by Eq. (3) are not evident in the film samples.

To further confirm these results, the above was repeated for a homoepitaxial silicon carbide thin film, where a 6H-SiC film of about 6  $\mu\text{m}$  was grown on a single crystal 6H-SiC SiC substrate. The measured electron distribution is plotted together with the calculated using Eqs. (1)–(3) in Fig. 4, where the two curves are almost identical to each other. It should be noted, however, that in this case there are nonvanishing phases, and they were taken from the calculated values for both curves.

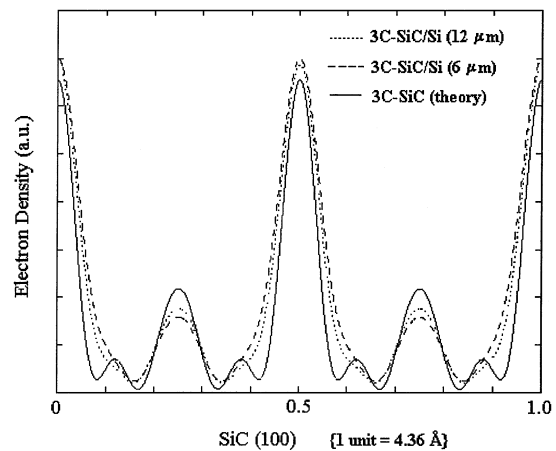


FIG. 3. Measured and calculated electron density maps of 3C-SiC along the surface normal.

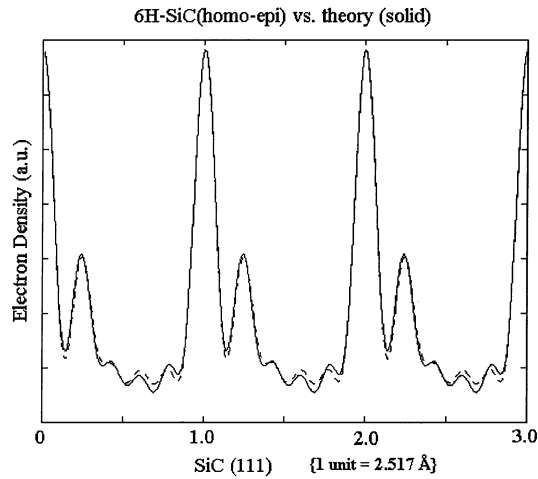


FIG. 4. Measured and calculated electron density maps of 6H-SiC along the surface normal.

Finally, it should be commented that the scheme presented here is based on the kinematic theory, which is just an approximation from the dynamic theory, suitable for large and perfect crystals. However, since we are dealing with highly roughened thin films, due to the presence of lattice mismatch, the kinematic approach gives a fairly good description, as shown by the good agreement between the experimental results and theoretical calculation.

To conclude, we have developed a new method to study the internal atomic arrangement of epitaxial materials by short wavelength x-ray diffraction. Applying to the case of cubic SiC films grown on Si(100) substrate, up to 5 order Bragg peaks along (100) have been measured and the crystallographic structure factors are obtained experimentally. Through this new method, we have achieved a quantitative characterization of the internal atomic layer roughness and distortion of heteroepitaxial 3C-SiC and homoepitaxial 6H-SiC thin films. It is found that the electron density distribution can be easily reconstructed, using short-wavelength x rays to measure high order Bragg reflections. Compared with the calculated values from atomic scattering factors, the deviation of the unit cell structure from the ideal case can be identified. Through a combination of theory and experiment this study provides a practical and useful method to investigate the other thin film materials and systems.

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- [1] J. A. Powell, P. Pirouz, and W. J. Choyke, in *Semiconductor Interfaces, Microstructures and Devices: Properties and Applications*, edited by Z. C. Feng (Institute of Physics Publishing, Bristol, 1993), p. 257.
- [2] R. F. Davis and J. T. Glass, *Adv. Solid State Chem.* **2**, 1 (1991).
- [3] *Properties of Silicon Carbide*, edited by Gary L. Harris, Electronic Materials Information Service (Institute of Electrical Engineers, United Kingdom, 1995).
- [4] S. Nishino, J. A. Powell, and H. A. Will, *Appl. Phys. Lett.* **42**, 460 (1983).
- [5] Y. M. Tairov and V. F. Tsvetkov, *J. Cryst. Growth* **43**, 209 (1978); **52**, 146 (1981).
- [6] J. A. Lily, *Ber. Dtsch. Keram. Ges.* **32**, 229 (1955).
- [7] W. J. Choyke, H. Matsunami, and G. Pensel, *Phys. Status Solidi (a)* **162** (1997); *Phys. Status Solidi (b)* **202** (1997).
- [8] Th. Kunstmann and S. Veprek, *Appl. Phys. Lett.* **67**, 3126 (1995).
- [9] C. A. Zorman, A. J. Fleischman, A. S. Dewa, M. Mehregany, C. Jacob, S. Nishino, and P. Pirouz, *J. Appl. Phys.* **78**, 5136 (1995).
- [10] K.-W. Lee, K.-S. Yu, J. W. Bae, and Y. Kim, *Mater. Sci. Forum* **264-268**, 175 (1998).
- [11] S. Miyagawa, S. Nakao, K. Saitoh, M. Ikeyama, H. Niwa, S. Tanemura, Y. Miyagawa, and K. Baba, *J. Appl. Phys.* **78**, 7018 (1995).
- [12] H. Weishart, W. Matz, and W. Skorupa, in *Silicon Carbide and Related Materials, 1995: Proceedings of the 6th International Conference, Kyoto, Japan*, edited by S. Nakashima, H. Matsunami, S. Yoshida, and H. Harima (IOP, Bristol, 1996), Ser. 142, p. 541.
- [13] A. Ellison, J. Di. Persio, and C. Brylinski, in Ref. [12], p. 441.
- [14] H. Romanus, G. Teichert, and L. Spiess, *Mater. Sci. Forum* **264-268**, 437 (1998).
- [15] V. Ivantsov and V. Dmitriev, *Mater. Sci. Forum* **264-268**, 73 (1998).
- [16] Z. J. Zhang, K. Narumi, H. Naramoto, S. Yamamoto, and A. Miyashita, *J. Phys. Condens. Matter.* **10**, 11 713 (1998).
- [17] S. Rendakova, V. Ivantsov, and V. Dmitriev, *Mater. Sci. Forum* **264-268**, 163 (1998).
- [18] C. Hallin, A. Ellison, I. G. Ivanov, A. Henry, N. T. Son, and E. Janzen, *Mater. Sci. Forum* **264-268**, 123 (1998).
- [19] S. Milita, R. Madar, J. Baruchel, and A. Mazuelas, *Mater. Sci. Forum* **264-268**, 29 (1998).
- [20] B. E. Warren, *X-Ray Diffraction* (Addison-Wesley, New York, 1969).
- [21] C. H. MacGillavry, K. Lonsdale, and G. D. Rieck, *International Table of X-Ray Crystallography* (The Kynoch Press, United Kingdom, 1968).