Reflection high-energy electron diffraction patterns of carbide-contaminated silicon surfaces

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Carbon contamination of silicon surfaces is a longstanding concern for growers of thin films who utilize silicon wafer substrates. This contamination often takes the form of epitaxial β-SiC particles which grow after the decomposition of adsorbed carbon-bearing molecules, and the subsequent reaction of the freed carbon with the silicon substrate. Positive identification of such SiC contamination is possible via reflection high-energy electron diffraction (RHEED). To provide a complete demonstration and analysis of the relevant RHEED patterns, we prepared within a "silicon molecular beam epitaxy" system carbide-contaminated silicon surfaces using procedures intended to foster such contamination. With conventional RHEED instrumentation, we obtained transmission electron diffraction patterns which resulted from the passage of the RHEED electron beam laterally *through* the SiC particles. Comparison with theoretically predicted patterns positively identifies the β-SiC phase and shows that the particles are epitaxially aligned, with their cubic axes parallel to those of the substrate. {This finding is in agreement with the widely accepted model for the behavior of carbon on silicon surfaces [Henderson *et al.*, J. Appl. Phys. **42**, 1208 (1971)]}. More typically during *in-situ* silicon substrate preparation for thin film growth, RHEED patterns indicating such contamination contain SiC spots which are mere vestiges of the complete transmission diffraction patterns presented in this work.

I. INTRODUCTION

The reproducible growth of the highest quality epitaxial thin films demands atomically clean substrate surfaces and, thus, the detection and elimination of surface contamination become essential to the experimentalist. With silicon substrates, the challenge is to remove native silicon dioxide, and carbon-bearing gas molecules which adsorb on the silicon surface as a result of exposure to the atmosphere, and to do so at minimal cost in time, effort, and materials.[1] If the carbonaceous species decompose on the surface, instead of desorbing intact, the resulting free carbon atoms may bond to the silicon surface particularly strongly in forming silicon carbide.[2,3]

A subsidiary challenge is simply the detection and identification of these surface contaminants, or conversely, the verification of an adequately clean silicon surface. The purpose of this article is to address part of this second challenge, the detection and positive identification of silicon carbide contamination as revealed with conventional reflection high-energy electron (RHEED) equipment, which has become a standard component for "Si molecular beam epitaxy (MBE)" deposition systems.

Figure 1 shows a RHEED pattern taken with the incident beam along one principal azimuth (the $\langle 110\rangle$) of a Si(111) surface; it is typical of patterns encountered by film growers which reveal SiC contamination. The specific indication is the presence of faint and broad spots positioned to the outside of the primary silicon streaks. (Other indications that at least *some* sort of surface contamination is present include the diffuse quality of the primary silicon streaks and the absence of higher order 7×7 surface reconstruction streaks.) Henderson *et al.* first interpreted such a pattern in this way, in 1970.[4] This picture of carbon contamination has been the prevailing one[5] for over 20 years; probable images of such SiC particles have been obtained recently with the scanning tunneling microscope.[6]

At the outset this interpretation is not at all obvious. One might reason that since the lattice parameter of face-centered-cubic β-SiC is about 20% smaller than that of silicon, the spacing of the carbide's reciprocal lattice rods should be enlarged by this amount (in rough agreement with what is seen in Fig. 1); however, we have not found in the literature to date any complete and convincing analysis of RHEED patterns like that of Fig. 1. (The most complete analysis is perhaps that of Menadue, published in 1972.[7]) By presenting in this paper more complete experimental diffraction patterns, and comparing them to theoretical patterns, we will show definitively that Fig. 1 is evidence of particles of β-SiC epitaxially aligned with the silicon substrate. This analysis will be performed for two principal azimuthal orientations of both 1–0–0 and 1–1–1 wafers.

II. EXPERIMENTAL PROCEDURES

The silicon substrates were 3 in. diam Monsanto Prime Grade wafers (1–0–0, n-type, 1–50 Ω cm, and 1–1–1, n-type, 1.6–2.4 Ω cm). The wafers were removed from the box, immersed in a commercially available semiconductor industry buffered HF solution [10:1 by volume solution of ammonium fluoride (40%) and hydrofluoric acid (49%)] for approximately 30 s and loaded immediately into the introduction chamber of our Si MBE growth system (base pressure in the 10^{-11} Torr range). This "HF-dip" is performed in order to remove native oxide which has accumulated during months' or even years' exposure to the atmosphere. This is the normal *ex situ* part of our substrate preparation procedure; it yields silicon substrate surfaces (both 1–0–0 and

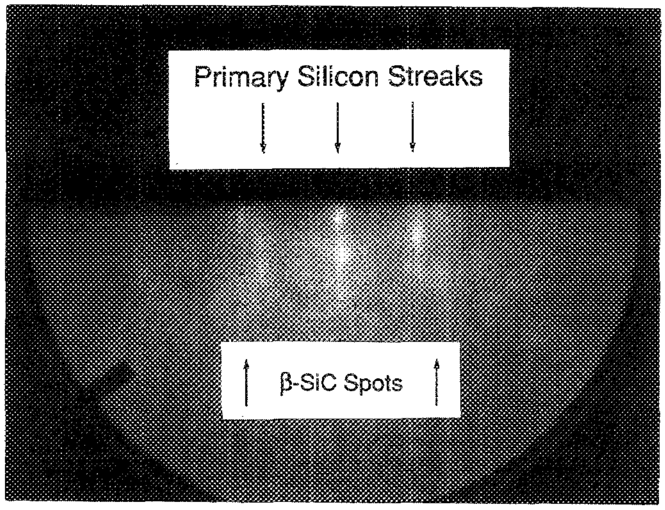


FIG. 1. Example of a RHEED streak pattern typically interpreted as revealing the contamination of a Si(111) surface by β-SiC. The incident beam is along a Si⟨110⟩ azimuthal direction. The diffraction spots auxiliary to the primary silicon streaks are evidence for the existence of epitaxial β-SiC particles.

1–1–1) which reconstruct at typically 350 °C and which exhibit *no* RHEED evidence of carbide contamination such as that illustrated in Fig. 1.

In the present work, special steps were undertaken in order to reproducibly prepare SiC-contaminated silicon wafer surfaces. In our deposition system the wafer is cradled in a machined molybdenum block. SiC contamination of the wafers was fostered by our deliberate usage of molybdenum blocks which had been exposed to the atmosphere for at least several days. Prior experience has indicated that these moly blocks must be outgassed at typically 1000 °C within the high vacuum MBE growth chamber before they are sufficiently clean for utilization in quality film growths. In the present work, since this preconditioning of the moly block was *not* performed, the desired surface contamination occurred as the sample and its moly block were heated together within the growth chamber.

Once within the system's growth chamber, the sample in its contaminated moly block was slowly brought to 400 °C. At this temperature, the expected two-domain 2×1 reconstructed RHEED pattern of the Si 1–0–0 wafers was visible on the RHEED screen, but in the case of the 1–1–1 wafers in this study, the 7×7 pattern was sometimes, but not always, obtained. With our standard procedures, we pause for 15 min at this temperature in an attempt to allow any carbon-bearing molecules which may have adsorbed on either the wafer or the (normally outgassed) moly block to desorb intact (at a temperature at which their decomposition on the surface is unlikely).

The previously stated rationale for such a desorption step was first presented, to our knowledge, by Delage *et al.*[8] Indeed, we see modest CO_2, CO, and C transients (along with H_2O, HO, O, and H_2) in our quadrupole residual gas analyzer (RGA) spectra during this 400 °C anneal. Presumably the concentration distributions of these related species are representative of the cracking pattern of the vapor within the RGA head and not of adsorbates on the substrate surface. According to our customary procedures, the substrate is then raised to 800 °C, the temperature at which we normally perform a "silicon beam clean."[9] With a properly outgassed moly block the chamber pressure will remain in the low 10^{-9} Torr range and the higher order silicon RHEED streaks persist, and even sharpen, during exposure to the light silicon flux.

However, in the present investigation each sample in its contaminated block was quickly raised to 800 °C without any pause at 400 °C, whereupon the chamber pressure rose to the high 10^{-8} Torr range. Any higher order (reconstructed) streaks disappeared from the silicon RHEED patterns, with only the silicon primary streaks remaining. The RGA spectra contained relatively large peaks for CO_2, CO, and C. Additional diffraction spots as in Fig. 1 appeared in the patterns.

To further develop the spot pattern, which we anticipated as being due to β-SiC, the temperature of some samples was raised at this point to either 900 or 1000 °C and held there for typically 5 min. During these high temperature treatments, the chamber pressure rose as high as 1×10^{-7} Torr; this is almost two orders of magnitude greater than normal and was due to additional outgassing from the moly block. A distinct and rather complete spot pattern appeared on the RHEED screen. Photographs of the RHEED screen were taken after cooling the sample to room temperature. One representative wafer was *ex situ* analyzed with x-ray photoemission spectroscopy (XPS). Binding energy analysis showed that a substantial portion of the carbon on the surface of this wafer existed in the form of silicon carbide.

III. EXPERIMENTAL RHEED PATTERNS

Figures 2 and 3 show experimental RHEED patterns taken along the two principal azimuthal orientations of Si(001) and (111) surfaces, respectively. The 1–0–0 wafer was taken to 900 °C and the 1–1–1, to 1000 °C in order to obtain these RHEED patterns.

These patterns exhibit a two-dimensional array of diffraction spots rather than the typical RHEED streaks or spots lying along circular arcs. Such a RHEED pattern is characteristic of a rough surface and is due to transmission diffraction through surface asperities.[10] We adopt the term "transmission RHEED" for this phenomenon of observing *transmission* electron diffraction patterns with conventional RHEED instrumentation, which by contrast is normally employed for obtaining *reflection* electron diffraction patterns. These patterns will be shown below to be experimental examples of transmission diffraction patterns of epitaxial β-SiC particles.

IV. THE EXPECTED TRANSMISSION RHEED PATTERNS OF β-SiC

The cubic form of silicon carbide is the zincblende crystal β-SiC, with a lattice constant of approximately 4.36 Å. The space group is F$\bar{4}$3m (No. 216). The conditions limiting possible reflections for this space group as listed in the *International Tables for X-ray Crystallography*[11] are

$$hkl:\quad h+k,\quad k+1,\quad (l+h)=2n.$$

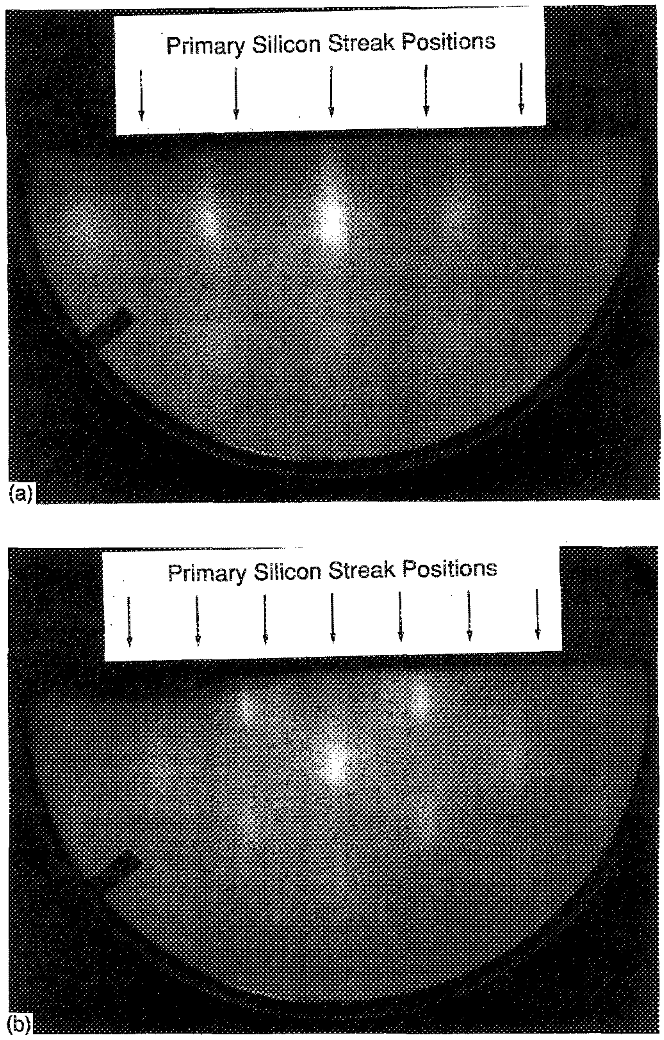


FIG. 2. Following procedures intended to foster SiC contamination, these experimental RHEED patterns were obtained from a Si(001) surface with incident beam along (a) Si⟨100⟩ and (b) Si⟨110⟩. The lateral positioning of primary silicon streaks is indicated for reference.

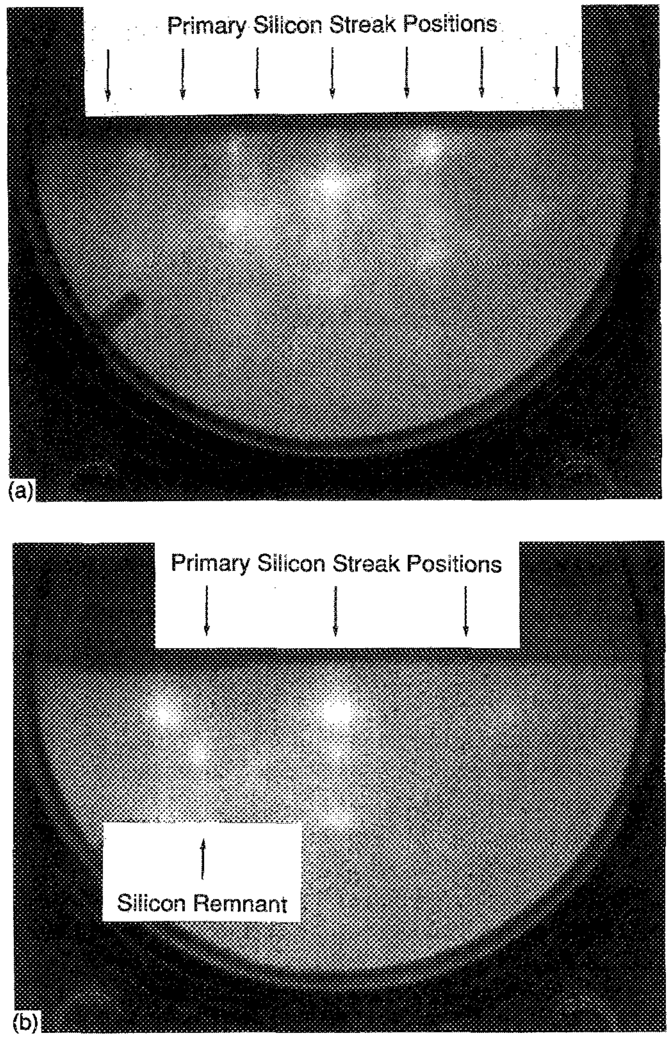


FIG. 3. Experimental RHEED patterns for a SiC-contaminated Si(111) surface along (a) Si⟨110⟩ and (b) Si⟨112⟩. In the latter pattern the remnant of a silicon streak is identified.

Using the above conditions and the general relation for cubic lattices specifying which reciprocal lattice points are contained in the plane section perpendicular to the incident beam of direction $[uvw]$, namely, $hu+kv+lw=0$, theoretical transmission electron diffraction patterns for β-SiC were generated. Figure 4 shows three such spot patterns along different beam directions.

These patterns were used to construct the possible *transmission* RHEED views displayed in Figs. 5 and 6, since *transmission* RHEED patterns were obtained experimentally in Figs. 2 and 3. The following heteroepitaxial relationships were assumed:

$$\beta\text{-SiC}(001)/\text{Si}(001) \quad \text{with} \quad \beta\text{-SiC}[110] \| \text{Si}\langle 110\rangle$$

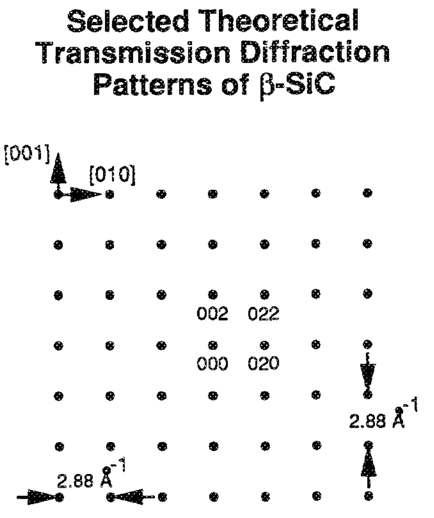
and

$$\beta\text{-SiC}(111)/\text{Si}(111) \quad \text{with} \quad \beta\text{-SiC}[\bar{1}10] \| \text{Si}\langle 110\rangle.$$

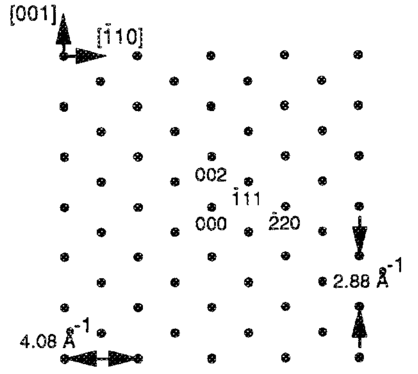
The real-space dimensions in Figs. 5 and 6 were determined with the camera equation, using an electron acceleration potential of 10 kV and a point of incidence-to-screen distance of 31 cm.[12] Primary silicon streak positions are superposed onto the β-SiC transmission RHEED patterns for reference. The calculated lateral positions of the primary streaks are in agreement with experiment to within ~0.2 mm.

V. POSITIVE IDENTIFICATION OF β-SiC CONTAMINATION

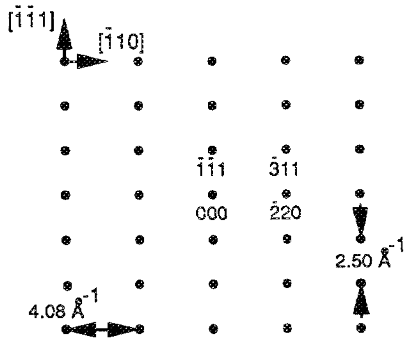
First, we will consider the transmission RHEED patterns which were presented in Figs. 2 and 3. There is an excellent correspondence in both form and size between the predicted views of β-SiC diffraction patterns presented in Figs. 5 and 6 and the arrays of diffraction spots seen in the experimental transmission RHEED patterns. This correspondence, in considering the deliberately contaminating procedures we used, the evidence of evolution of carbon-bearing molecules in the RGA spectra, the auxiliary chemical analysis afforded by x-ray photoelectron spectroscopy (XPS), and the extreme repeatability with which β-SiC has been found to occur over



a) Beam Along β-SiC [100]



b) Beam Along β-SiC [110]



c) Beam Along β-SiC [112]

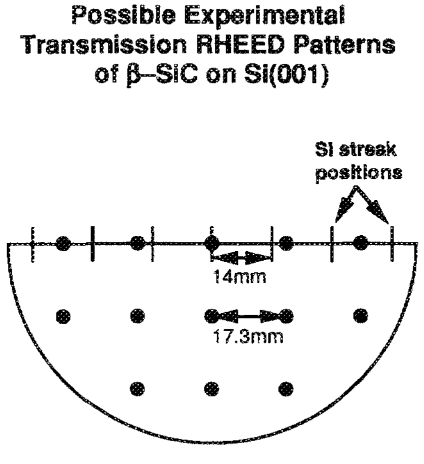
FIG. 4. Theoretical transmission electron diffraction patterns of β-SiC with incident beam along (a) β-SiC[100] (b) β-SiC[110], and (c) β-SiC[112].

the years, allows us to attach a high degree of confidence to this β-SiC phase identification via the transmission RHEED patterns.

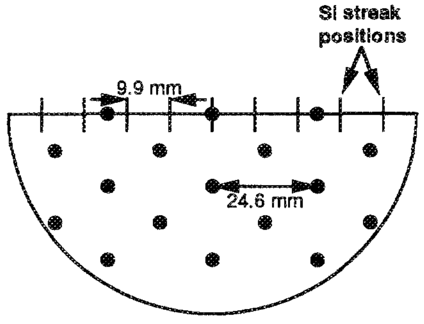
There is one experimental case [Fig. 3(b)] where a *composite* (β-SiC plus Si) pattern is seen. On the left-hand side of this photograph there is the remnant of one silicon streak which rests amid the β-SiC spot pattern. This silicon feature can be easily distinguished from those of β-SiC due to the almost 20% difference in reciprocal lattice parameters, as portrayed in the theoretical composite pattern of Fig. 6(b).

We return now to the more typical experimental RHEED pattern of a β-SiC-contaminated surface presented in Fig. 1. The dominant features are three fundamental streaks of the Si(111) surface. Carbide contamination is revealed by the fuzzy auxiliary spots to the outside of the silicon streaks. These fuzzy spots are remnants of two predicted β-SiC spots in Fig. 6(a). We would suggest that they are relatively dim and broad because the β-SiC particles are not, in some sense, as well-formed on this sample. Nevertheless, the complete analysis presented above shows that patterns such as Fig. 1 are indicative of carbon contamination in the form of epitaxial β-SiC.

Clearly, there are differences among our samples in the degree of substrate surface coverage by carbide and in the structural quality of the epitaxial β-SiC particles themselves. Figure 1 is dominated by silicon primary streaks and contains only two fuzzy β-SiC spots which are but vestiges of the complete transmission diffraction pattern. This sample was heated to only 800 °C. Figures 2 and 3 were obtained from surfaces which had been annealed at either 900 or 1000 °C for the express purpose of enhancing the size, structural perfection, and epitaxial alignment of the β-SiC crystallites. The quality of the diffraction patterns suggests that some sort of enhancement indeed occurred, especially in Fig.



a) Along β-SiC<100>



b) Along β-SiC<110>

FIG. 5. Expected transmission RHEED patterns of epitaxial β-SiC particles on Si(001) along (a) Si$\langle 100\rangle$ and (b) Si$\langle 110\rangle$. Because of the heteroepitaxial relationship between the two crystals, these views are also along (a) β-SiC$\langle 100\rangle$ and (b) β-SiC$\langle 110\rangle$. The theoretical positions of the primary silicon streaks are indicated; lateral positions of all the diffraction features were calculated with the camera equation.

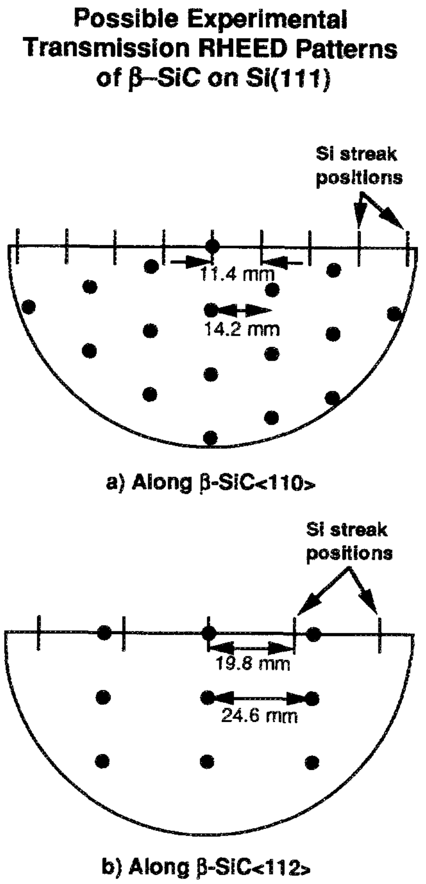


FIG. 6. Expected transmission RHEED patterns of epitaxial β-SiC particles on Si(111) along (a) Si⟨110⟩ and Si⟨112⟩ or, equivalently, along (a) β-SiC⟨110⟩ and (b) β-SiC⟨112⟩.

2, which contains relatively sharp β-SiC diffraction spots. Figure 3(b) is dominated by β-SiC transmission spots but still contains a silicon feature. In spite of these differences, all cases can be analyzed with the aid of the predicted transmission RHEED patterns of Figs. 5 and 6.

VI. SUMMARY AND CONCLUSIONS

The purpose of this article is to present complete experimental and theoretical RHEED analysis of a widely observed form of carbon contamination of Si(001) and (111) surfaces: epitaxial β-SiC particles whose cubic axes are parallel to those of the silicon substrate. While this has been the traditional expectation for and interpretation of carbon contamination of these surfaces for over 20 years, a complete RHEED analysis has been lacking in the reference literature.

To summarize our procedures and results, we prepared silicon (001) and (111) surfaces which were deliberately contaminated with carbon by outgassing of carbonaceous species from a substrate holder. Epitaxial β-SiC particles were formed on these surfaces by heating the substrates to 800 °C under modestly high vacuum, resulting in RHEED patterns which were typically composed of primary silicon streaks plus diffuse spots not attributable to silicon. Higher temperature anneals (900 or 1000 °C) produced relatively sharp transmission RHEED patterns, which were presumably due to an enhanced crystallinity and/or size of the epitaxial β-SiC particles.

These sharp spot patterns are not typical of β-SiC contamination often observed with RHEED by thin film growers. Our *composite* experimental RHEED pattern of Fig. 1 (containing silicon primary streaks plus only two fuzzy β-SiC spots) is more representative of typical surface preparation failures resulting in carbide contamination. Nevertheless, investigators may utilize the RHEED analysis presented in this paper to positively identify RHEED features which owe their origin to epitaxial β-SiC particles, the most common form of carbon contamination of silicon substrates in MBE growth.

ACKNOWLEDGMENT

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