SURFACE SCIENCE LETTERS

ELEMENTAL COMPOSITION OF $\beta$-SiC(001) SURFACE PHASES STUDIED BY MEDIUM ENERGY ION SCATTERING

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$\beta$-SiC surfaces have been investigated in terms of surface composition and reconstruction by medium energy ion scattering (MEIS), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED). A (3 x 2) phase is produced by evaporating Si on a $\beta$-SiC surface. Heat treatment at 1065°C causes consecutive transformation into (5 x 2), c(4 x 2), (2 x 1), (1 x 1) and c(2 x 2) phases. Quantitative analysis of MEIS spectra shows that the c(4 x 2) surface has a full silicon topmost layer, whereas the c(2 x 2) surface has a full carbon topmost layer. The (3 x 2) and (5 x 2) phases are believed to originate from additional Si dimer rows on top of a Si terminated crystal.

SiC, as a semiconducting material with a high melting point and a wide bandgap, seems a suitable candidate for replacement of silicon in specific high temperature applications and in radioactive ambiances. Although many efforts were directed towards using $\alpha$-SiC for electronic devices [1], little advance was made because of the unfitness of $\alpha$-SiC for mass production. On the other hand, the growth of $\beta$-SiC (3C-SiC) crystals has recently been improved by the development of a new chemical vapor deposition (CVD) technique [2,3]. $\beta$-SiC has a zincblende structure, with Si and C planes alternating in the (001) direction. The high crystal quality of $\beta$-SiC has raised scientific interest [4–7] and has stimulated research in device applications [8–12].

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In the past years various investigations have been made of the structure and composition of SiC surfaces [13–19]. Such studies contribute to our understanding of the electrical properties of metal/SiC interfaces. Bellina and Zeller have found by AES [17] that the $\beta$-SiC(001) surface has a variable atomic composition, the amount of Si and C depending on heat treatment. Dayan has observed three different LEED patterns on the SiC(001) surface, namely (3 x 2), (2 x 1), and c(2 x 2). Each pattern corresponds to a different composition [14–16]. It was suggested that heat treatment causes an increase in carbon concentration at the $\beta$-SiC surface. Recently, Kaplan [18] formed a silicon-rich surface on $\beta$-SiC samples by UHV deposition of Si and found in his AES and electron energy loss spectroscopy experiments [19] that these phases transform reversibly into one another by appropriate choice of sample temperature and silicon flux.

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In this Letter, we report a medium-energy ion scattering (MEIS) investigation of the β-SiC(001) surface. When used in combination with channeling and blocking, MEIS provides information on surface structure and composition. Details of the experimental method and set-up have been discussed elsewhere [20]. In the present experiment, H\textsuperscript+ ions of 98.7 keV energy are incident along the [11\bar{1}] channeling direction. Backscattered ions are collected by a toroidal electrostatic analyzer, permitting simultaneous detection of ions with a 20° range of exit angles. The energy resolution of the analyzer is $\Delta E/E = 3.6 \times 10^{-3}$ [21].

Sample cleaning and backscattering analysis were performed in an ultrahigh-vacuum chamber (base pressure $7 \times 10^{-9}$ Pa) connected to a loading chamber and a UHV chamber for molecular beam epitaxy (MBE). The MBE chamber contains a Si e-gun evaporator and is equipped with a reflection high energy electron diffraction (RHEED) facility. The analysis chamber is coupled to a 200 kV ion accelerator, and is equipped with a 5-grid LEED system and a cylindrical mirror analyzer (CMA) with a coaxial gun for AES. Samples were heated resistively, while the temperatures were monitored with an optical pyrometer.

Single crystal layers of β-SiC were grown in a CVD reactor on a boron-doped Si(001) substrate at 1350°C for 3 h using C\textsubscript{2}H\textsubscript{2}, SiH\textsubscript{4} and H\textsubscript{2} gases onto a carbonized buffer layer made from C\textsubscript{3}H\textsubscript{8} and H\textsubscript{2} [22]. The thickness of the SiC layers was about 7 μm. The sample surface was cleaned in situ in the Si MBE chamber by letting the surface react at 900°C with an incident flux of Si atoms. This procedure is known to lead to desorption of surface oxides [18]. Prior to Si deposition, the substrate was degassed by raising its temperature to 700°C for 10 min. The degassed sample showed a (1 × 1) pattern by RHEED. Si was deposited at a rate of 0.15 nm/min. During the Si deposition, the (1 × 1) RHEED pattern gradually converted into a (2 × 1) pattern after 1.5 min, and a (3 × 2) pattern after 3.5 min. Si evaporation was then stopped and the substrate temperature was decreased to room temperature. LEED showed a clear (3 × 2) pattern with streaked 1/2 order spots (fig. 1a). Heating causes the appearance of a sequence of reconstructions (fig. 2). A clear (5 × 2) pattern (fig. 1b), with the 1/2 order spots merged into a line, appeared by annealing the (3 × 2) surface at 1065°C for 4 min. A (5 × 2) phase on β-SiC has not been reported before in the literature. An additional anneal at 1065°C for 2 min resulted in a sharp c(4 × 2) pattern, but leaving the c(4 × 2) surface at room temperature for 12 h resulted in a (2 × 1) pattern. Annealing of the
(2 × 1) surface at 1065°C for 6 min converted it into a (1 × 1), and additional annealing for 8 min resulted in a c(2 × 2) pattern. Although the series of the reconstructions from a (3 × 2) to a c(2 × 2) was observed consecutively, a certain reconstruction appeared only in a narrow range of surface composition for each reconstruction. Just after each clear LEED pattern was observed the surface temperature was reduced rapidly to room temperature in order to take a MEIS spectrum, and subsequently raised to 1065°C again. Ion scattering spectra showed all the surfaces to be free of oxygen and Auger electron spectra exhibited no O(KLL) signal.

All patterns include 90° rotated domains. It is reported that in the case of heteroepitaxial growth of a polar β-SiC crystal on a nonpolar Si substrate, steps with monoatomic layer height on the substrate generate antiphase boundaries in the grown film [23–25]. Therefore the two-domain LEED patterns must originate from the anti-phase domains in the bulk SiC layers.

The Si(LVV)/C(KLL) Auger intensity ratios, not corrected for the energy-dependent transmission of the CMA, are 4.3, 4.3, and 1.5 for the (3 × 2), c(4 × 2), and c(2 × 2) surfaces, respectively. This indicates that the surface changes from Si-rich to C-rich upon annealing. Kaplan has observed on the (3 × 2) surface a Si(LVV) derivative signal with a peak split in two components [18]. In our Auger measurement, the Si(LVV) derivative peak for the (3 × 2) surface was broader than the peak for the c(2 × 2) surface, which is consistent with Kaplan’s observation.

Fig. 3 shows Si and C backscattering peaks measured in double alignment (the incidence and exit angles are aligned with the [111] and [111] directions of the SiC(001) crystal, respectively). The ion shadowing and blocking effects which then occur result in a high surface sensitivity [20]. The spectra directly show the C enrichment which occurs when the LEED pattern changes from a (3 × 2) to a c(2 × 2) structure; the C peak has a higher intensity for the c(2 × 2) surface than for the (3 × 2) surface while the Si peak has a lower intensity for the c(2 × 2) surface. Furthermore, the Si peak for the (3 × 2) surface is at the energy calculated for elastically backscattered ions (verti-
cal lines in fig. 3), whereas the corresponding C peak is at a slightly lower energy. The latter implies that the \((3 \times 2)\) surface is Si terminated. The Si termination layer causes a shift of the C peak to lower energies because of inelastic energy losses of the \(H^+\) ions in the Si layer. The backscatter peaks for the \((c(2 \times 2))\) surface show consistent behavior (fig. 3). In this case the C peak is at the elastic energy while the Si peak has shifted slightly to a lower energy. Hence the \((c(2 \times 2))\) surface is C terminated.

The area of the surface peaks in figs. 3a and 3b has been converted into the areal density of atoms visible to the ion beam and detector using a standard calibration procedure [20]. Fig. 2 shows the areas of the Si and C backscatter peaks expressed in monolayers as a function of annealing time at 1065°C (one monolayer is defined as the areal density of atoms in a single SiC(001) plane and equals \(1.05 \times 10^{15}\) atoms/cm²). In the figure a comparison is made with computer simulated yields [26] for bulk-like SiC surfaces with either a Si or a C termination (hatched areas). In the simulation the Si and C atoms were assumed to vibrate uncorrelated with a one-dimensional rms amplitude in the range of 0.08 to 0.10 Å. The simulations, though they do not account for reconstruction induced static displacements, provide an additional, quantitative criterion for determining the terminating element at the surface. The \((3 \times 2)\), \((5 \times 2)\) and \((c(4 \times 2))\) surfaces are seen to be all Si terminated, with the \((c(4 \times 2))\) surface giving Si and C yields closest to the simulated yields. By contrast, the observed Si and C yields for the \((c(2 \times 2))\) surface can only be accounted for by C termination.

From LEED and AES studies Kaplan [19] concluded that the \((3 \times 2)\) structure arises from additional Si on top of the Si-terminated \((c(4 \times 2))\) surface. This is consistent with our observation of a \((3 \times 2)\) surface having excess Si on top of a Si terminated \((c(4 \times 2))\) surface.

The \((c(4 \times 2))\) reconstruction is likely to have the same geometry as the reconstructions of Si(001) surfaces, i.e., the surface is covered with an array of asymmetric dimers [27]. In analogy with spin arrangements various asymmetric dimer configurations are possible. The antiferromagnetically (AF) ordered spin phase is apparently the most stable one since this gives rise to a \((c(4 \times 2))\) pattern [19]. The phase transformation from a \((c(4 \times 2))\) AF into a \((2 \times 1)\) ferromagnetic (F) phase at room temperature indicates that the energy gain upon ordering into an AF configuration is only minor. The AES and MEIS spectra from the \((c(4 \times 2))\) and \((2 \times 1)\) surfaces were identical, implying that these two have very similar structure and composition.

The structure model proposed by Kaplan [19] and Dayan [16] for the \((3 \times 2)\) phase involves rows of Si dimers on top of the Si terminated crystal, with a vacancy row every third row. This model which corresponds with a \(2/3\) monolayer coverage of excess Si, is inconsistent with our observation of only \(1/3\) monolayer of excess Si. Also our observation of a \((5 \times 2)\) phase which is intermediate between \((3 \times 2)\) and \((c(4 \times 2))\) does not provide support for this vacancy model. A \((5 \times 2)\) surface would then have a vacancy row every fifth row and thus would be more Si-rich than \((3 \times 2)\), which is in contradiction to our data. Instead, we propose a model for the \((n \times 2)\) phases in which every \(n\)th row of dimers is present between \(n - 1\) vacancy rows in the direction normal to the dimers. This makes a \((5 \times 2)\) surface less Si-rich than a \((3 \times 2)\) surface. For an \((n \times 2)\) phase to exist, a ferromagnetic ordering of the asymmetric dimers is required. The streaking of the \(1/2\) order spots in the \((3 \times 2)\) phase is thought to originate from a loss of the ferromagnetic ordering of the dimer rows [19]. The much more pronounced streaking observed by us in the \((5 \times 2)\) pattern strongly indicates that such a disordering is caused by a decoupling of the dimer rows; in a \((5 \times 2)\) structure the decoupling will be stronger than for a \((3 \times 2)\) structure, since the distance between dimer rows is twice as large for a \((5 \times 2)\) surface. From this model we predict the existence of a \((7 \times 2)\) phase intermediate between \((5 \times 2)\) and \((c(4 \times 2))\), which may be observed by an appropriate choice of annealing time and temperature.

The \((c(2 \times 2))\) surface has been believed to be covered with a full silicon layer [14] or half a silicon layer [18,19]. Above, it has been argued that the \((c(2 \times 2))\) surface is terminated with a monolayer of C. This assignment is also supported
by the relatively long annealing times required for transforming a (2×1) phase into a c(2×2) phase. Other experiments involving Ni depositions on a c(2×2) SiC surface [7] also gave evidence for C termination. A fully C terminated c(2×2) structure possibly consists of a c(2×2) arrangement of asymmetric C dimers.

The observation of a (1×1) phase, half-way in annealing time between the (2×1) and c(2×2) phases indicates an absence of dimers when the surface is terminated with roughly half a monolayer of C. We finally note that the Si(001) [28,29], Ge(001) [30], and GaAs(001) [31,32] surfaces which all have dimer reconstructions, do not display a c(2×2) phase. Thus the c(2×2) phase of β-SiC is exceptional probably owing to the shorter length of the C–C bond with respect to the substrate bond lengths.

In conclusion, we have investigated (3×2), (5×2), c(4×2), (2×1), (1×1), and c(2×2) reconstructions on β-SiC(001) using MEIS, AES, and LEED. It was found that the c(4×2) surface is terminated with a full silicon layer and that the c(2×2) surface is terminated with a full carbon layer. A new type of vacancy row model is proposed for the (3×2) and (5×2) phases. It consists of a Si dimer row on top of a Si terminated crystal every third or fifth row, respectively. The c(2×2) phase is proposed to consist of a full monolayer of dimerized C atoms.

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