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Structural and electronic properties of clean and defected Si-SiC(001) surfaces

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Abstract

We have studied the reconstructions and electronic properties of both clean and defected Si-terminated (001) surfaces of cubic SiC, by performing first principles computations within density functional theory. We find that the unstrained bulk exhibits a stable p(2x1) reconstruction, whereas a bulk under tensile stress shows a c(4x2) reconstruction. Furthermore our calculations indicate that ad-dimers are common defects on the Si-terminated SiC(001) surface. These results permit the interpretation of recent STM and X-ray-photoemission experimental data.

A Introduction

The characterization of SiC surfaces is an essential prerequisite to understanding the growth of Silicon Carbide, as well as its applications as a semiconductor for high-power, high-temperature and high-radiation environments [1].

Here we focus on the Si-terminated (001) surface of the cubic polytype of SiC (β-SiC), which is one of the most studied surfaces, although not yet well characterized [2]. There are two main issues which need to be addressed in order to understand the physical properties of SiC surfaces: (i) the influence of stress on the surface reconstruction and (ii) the modifications introduced by defects on the surface structure and electronic properties. Stress effects on cubic SiC surfaces represent a key issue since cubic SiC films are presently prepared by chemical vapor deposition on Si(001) substrates. The lattice mismatch between Si and SiC is almost 20 %, and thus SiC samples grown on Si are expected to be strained. Furthemore stoichiometric Si-terminated SiC(001) surfaces are prepared by evaporating excess-Si, and the presence of defects such as missing- and ad-dimers and missing- and ad-atoms is expected on the surface. The presence of defects on Si-SiC(001) is clearly visible from STM images [3] although the type of defects has not yet been identified.

In this paper we report about theoretical studies of the influence of stress (section B) and defects (section C) on the properties of Si-SiC(001). Our investigations have been carried out by performing a series of ab-initio molecular dynamics calculations within the local density functional approximation, using pseudopotentials and plane wave basis sets [4,5].

B Clean Si-terminated surface

Experimentally both p(2x1) [2] and c(4x2) [2,3] patterns have been observed on clean Si-SiC(001), with p(2x1) reconstructions being often seen in areas of missing dimers [3] and low coverage. The results of our calculations show that an unstrained bulk exhibits a p(2x1) reconstruction, which is under tensile stress. In agreement with Sabisch et al. [6], we have found that the p(2x1) reconstruction is characterized by dimer rows, with dimers much longer (2.6 Å) than those of Si(001) ($\simeq$ 2.3Å). These dimers are weakly bonded, with no important hybridization involved. The presence of weak bonds on the surface has not been confirmed experimentally, and the only fit to LEED data available in the literature points at shorter dimers [7]. However very recent ARUPS data [8] are consistent with models implying a weak bonding of the Si dimers. In our calculations we found that the p(2x1) reconstructed surface is non metallic at least up to 400 K. The surface has a gap between π^*-like antibonding states and σ bonding states. This is different from the electronic structure of the Si(001) and C(001) surfaces where the reconstruction opens a band gap between π and π^* surface states.

When applying small stresses to the cubic SiC bulk, we have observed a symmetry breaking of the surface reconstruction, leading to a c(4x2) pattern [4]. In our calculation, the c(4x2) surface geometry is characterized by alternating unbuckled short and long dimers, the short dimers having a component perpendicular to the surface smaller than the long ones. The dimer bond lengths are 2.54 and 2.62 Å in the case, e.g., of a 3 % strained bulk. This surface geometry is in agreement with the alternating-up-and-down-dimer (AUDD) model proposed on the basis of STM experiments [3]. Similarly to the p(2x1) reconstruction, the c(4x2) geometry exhibits a gap between antibonding occupied and bonding empty surface states.

Calculated STM images for both p(2x1) and c(4x2) reconstructed surfaces are displayed in Fig. 1. The top panels display the derivative of the tunneling current with respect to applied voltage: these images clearly show the π-like bonding states on the dimers. Bright spots appear on all dimers of the p(2x1) dimer rows (left), on the contrary only the up dimers are visible on the c(4x2) rows (right). Constant current plots at V=-1.5 eV (lower panels of Fig. 1) show instead surface states having large components *between* dimers. These are bonding and antibonding π-like states. On the p(2x1) surface bright spots are identical on all dimers, while on the c(4x2) surface they clearly show the difference in height between up and down dimers. When lowering the voltage from -1.5 to -3 eV in constant current plots, we found spots localized also on dimers, showing the difference in height between up and down dimers for the c(4x2) reconstruction. As expected, lowering the voltage makes the bonding π states have a larger contribution to the tunneling current. The image at V= -3 eV is in satisfactory agreement with measured [3] images at constant current, at the same voltage. However the measured images show larger components on dimers, indicating that in

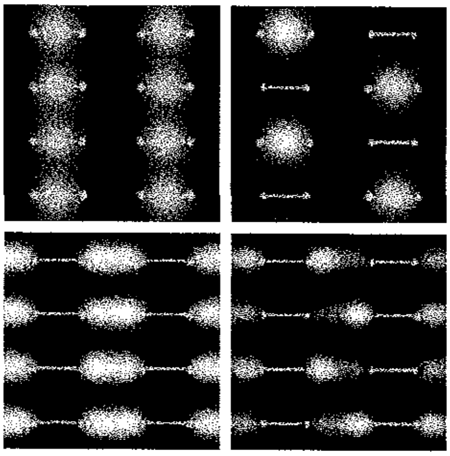

Figure 1 Computed STM images of the p(2x1) (left panel) and c(4x2) (right panel) reconstructions of Si-SiC (001). the upper and lower panels show a plot of $\frac{\partial I(x,y,z_0;V)}{\partial V} \propto \Sigma_i|\psi_i(x,y,z_0)|^2 f'(\epsilon_i+eV)$ (see text) and $I(x,y,z,V)=I_0$, respectively, in both cases V=-1.5 eV. Here $I(x,y,z;V)$ is the tunneling current computed within the Tersoff-Hamman approximation [10] at a given applied voltage V, the plot $I=I_0$ is drawn by considering all z values between the surface and the top of the slab such that $I=I_0$
. From Ref [4]

our calculation of $I(x,y,z,V)$, antibonding components of surface states are weighted more than experimentally This difference between theory and experiment may be related to the tip induced electric field, which could change the energy separation between π and π^* surface states

B Defected Si-terminated surfaces

In order to make contacts with several experimental results indicating the presence of defects on Si-terminated surfaces [2], we have studied the structural modifications induced by point defects on the surface structure.

Since p(2x1) reconstructions of Si-SiC(001) have been often seen in areas of missing dimers [3], we first investigated a p(2x1) reconstructed surface with missing dimers. We found that the removal of a dimer relieves surface stress and induces the formation of stronger bonds in four dimers surrounding the missing unit [4]. Nevertheless a dimer removal does not constitute a long ranged perturbation on the p(2x1) reconstruction, whose symmetry and dimer bond lengths are basically unchanged The computed surface core level shifts (SCLS) [5] of atoms close to the missing dimer are similar to those of surface atoms on clean substrates (0 9 eV, in our calculation), and vary between 0 8 and 1.1 eV.

We then considered an ad-atom and optimized two different surface geometries, with an extra atom between and on top of dimer rows, respectively The configuration of minimum energy corresponds to the adatom sitting between rows, forming four long (2.50 Å), equivalent backbonds with the surface atoms. The SCLS of the adatom — computed in the configuration of minimum energy — is very low ($\simeq$ 0.2 eV), compared to that of surface atoms.

Finally we considered ad-dimers on a p(2x1) terminated surface, and were inspired by recent investigations [9] of surfaces with excess Si atoms in order to determine a stable ad-dimer geometry. We have considered an ad-dimer *between* rows and optimized the total energy for geometries parallel and perpendicular to the p(2x1) dimer rows. We have found that the perpendicular ad-dimer has a total energy about 0.6 eV lower than the parallel one, and we have computed the SCLS for the configuration of minimum energy. The chemical shifts of atoms belonging to an ad-dimer are larger than those of surface atoms, i.e. $\simeq$ 1.4 eV higher in energy than the bulk value. We note that the ad-dimer bond length is much smaller than those of surface dimers, 2.28 Å, and thus the chemical bond of the ad-dimer is expected to be rather different from that of the weak, much longer surface dimers.

Si-2p spectra [10] obtained in X-ray photoemission experiments show the presence of two peaks, a main peak (S) and a much less intense feature (S') centered at 0.5-0.7 eV and 1.2-1.7 eV above the bulk contribution, respectively. In view of the results discussed above for SCLS, we have suggested that while surface atoms are responsible for the main peak (S) observed experimentally in X-ray photoemission spectra, ad-dimers are responsible for the less intense S' feature. Our results [5] point at ad-dimers as common defects on Si-SiC(001) surfaces.

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