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Core-level shifts of the $c(8 \times 2)$-reconstructed InAs(1 0 0) and InSb(1 0 0) surfaces

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ABSTRACT

We have studied In-stabilized $c(8 \times 2)$-reconstructed InAs(1 0 0) and InSb(1 0 0) semiconductor surfaces, which play a key role in growing improved III–V interfaces for electronics devices, by core-level photoelectron spectroscopy and first-principles calculations. The calculated surface core-level shifts (SCLSs) for the ζ and ζa models, which have been previously established to describe the atomic structures of the III–V(1 0 0)$c(8 \times 2)$ surfaces, yield hitherto not reported interpretation for the As 3d, In 4d, and Sb 4d core-level spectra of the III–V(1 0 0)$c(8 \times 2)$ surfaces, concerning the number and origins of SCLSs. The fitting analysis of the measured spectra with the calculated ζ and ζa SCLS values shows that the InSb spectra are reproduced by the ζ SCLSs better than by the ζa SCLSs. Interestingly, the ζa fits agree better with the InAs spectra than the ζ fits do, indicating that the ζa model describes the InAs surface better than the InSb surface. These results are in agreement with previous X-ray diffraction data. Furthermore, an introduction of the complete-screening model, which includes both the initial and final state effects, does not improve the fitting of the InSb spectra, proposing the suitability of the initial-state model for the SCLSs of the III–V(1 0 0)$c(8 \times 2)$ surfaces. The found SCLSs are discussed with the ab initio on-site charges.

1. Introduction

Producing In-stabilized $c(8 \times 2)$-reconstructed (1 0 0) substrate on the heteroepitaxial III–V growth front (e.g., InP/InGaAs and InAs/GaSb) has been found to improve the properties of these interfaces for electronics devices [1–5]. This III–V(1 0 0)$c(8 \times 2)$ surface is also a potential starting substrate for producing insulator/III–V interfaces for future metal–insulator–semiconductor (MIS) transistors [6,7]. Furthermore, the $c(8 \times 2)$ reconstruction has been used as the template to prepare organic–inorganic semiconductor interfaces [8]. To understand reasons for the beneficial effects of the $c(8 \times 2)$ reconstructions and to controllably utilize these reconstructions, it is essential to know the properties of the III–V(1 0 0)$c(8 \times 2)$ surfaces.

The III–V(1 0 0)$c(8 \times 2)$ surface has been found to be composed of unique ζ building blocks [9–16], which include dimers in the subsurface rather than top layer, monomer rows, and partially occupied atomic sites. Their "borderline" atomic configurations, labeled here ζ and ζa, with the 0% (for ζ) and 100% (for ζa) occupations [10] of the both atomic sites 1* and 6* are shown in Fig. 1. The ζ and ζa (4×2) cells, of which relative shift along the [0 1 1] direction causes the $c(8 \times 2)$ periodicity, provide an established basis to model the III–V(1 0 0)$c(8 \times 2)$ properties since depending on the surface preparation, both ζ and ζa areas have been

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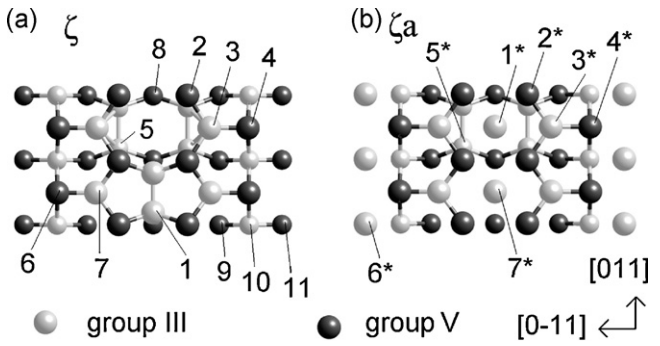

Fig. 1. (4×2) atomic models for the III–V(1 0 0)$c(8 \times 2)$-ζ and -ζa surfaces.

found without significant disorder related to the partial occupancy [9–16].

Surface core-level shifts (SCLSs) of the III–V(1 0 0)$c(8 \times 2)$, which are binding energy (BE) differences of the core-level photoelectrons emitted from the surface and deeper bulk atoms, have still remained an unresolved issue. In general, the knowledge of SCLSs is important for understanding the surface structures and interface formation as well as adsorption phenomena [5,17–24]. Mainly due to the lack of theoretical ab initio analysis of the SCLSs, the number of SCLSs and their physical origins for the III–V(1 0 0)$c(8 \times 2)$ surface have remained unclear.

To elucidate these issues, we have studied the InAs- and InSb(1 0 0)$c(8 \times 2)$ surfaces by core-level photoelectron spectroscopy and first-principles calculations. The obtained results are presented and discussed in this paper. The calculations for the established ζ and ζa models reveal several hitherto not reported SCLSs for the III–V(1 0 0)$c(8 \times 2)$ and clarify the origins of these SCLSs. The fitting analysis of the measured As 3d, In 4d, and Sb 4d spectra with the calculated ζa and ζ SCLS values shows that the InSb spectra are reproduced by the ζ SCLSs better than by the ζa SCLSs. On the contrary, the ζa fits agree better with the InAs spectra than the ζ fits do, indicating that the ζa model describes the InAs surface better than the InSb surface. These results agree with the previous X-ray diffraction analysis [10] showing almost complete (100%) and clearly lower occupancies for the ζa sites on the InAs- and InSb(1 0 0)$c(8 \times 2)$, respectively. Furthermore, the complete-screening ζ SCLSs, which include both the initial and final state effects, do not improve the present InSb fittings as compared to the initial state one, proposing the suitability of the initial-state model for the SCLSs of the III–V(1 0 0)$c(8 \times 2)$ surfaces. The found SCLSs are discussed with the ab initio on-site charges.

2. Experiments

Synchrotron radiation photoelectron spectroscopy measurements were done at the MAX-lab in Sweden at the beamlines 41 (InAs and InSb samples) and I511 (InAs). A hemispherical analyzer with an acceptance angle of about 2° was used at the beamline 41. The I511 is an undulator-based beamline equipped with a Scienta SES-200 hemispherical analyzer. The incident beam angle was 45° (7°) relative to the surface at the beamline 41 (I511). All measurements were done at room temperature. The photoemission ultrahigh vacuum (UHV) chamber was equipped with low-energy-electron-diffraction (LEED) and sputtering instruments.

Samples were n-type InAs(1 0 0) and InSb(1 0 0) wafer pieces. They were cleaned by argon-ion sputtering (1.5 keV, 10 mA) for 0.5 h at substrate temperature of about 300 °C and subsequent heating to 470 °C and 440 °C, respectively, in UHV for 0.5 h. Repeating such cycle four and six times produced sharp and established $c(8 \times 2)/(4 \times 2)$ LEED patterns (Fig. 2) from InAs- and InSb, respectively, as well as the In 4d spectra without any In-oxide and In-droplet related emissions. The LEED patterns in Fig. 2 reveal that the 2× order is better on the InSb- than on InAs(1 0 0)$c(8 \times 2)$ surface since the 2× LEED streaks of the latter suggest some stacking disorder in the 2× direction on the InAs(1 0 0)$c(8 \times 2)$ surface.

3. Calculations

The calculations were performed using the ab initio density functional total energy code with the local density approximation [25,26]. The approach is based on the plane wave basis and projector augmented wave method [27,28] (Vienna ab initio simulation package, VASP) [29–32]. The reconstructions in Fig. 1 were simulated by (4×2) slabs, including 17 atomic layers and treating the d electrons as core electrons. The (8×2) slabs were also used to simulate the experimentally found $c(8 \times 2)$ structure, but differences between the results obtained by different slabs are marginal. The optimization of the atomic structure was performed using conjugate-gradient minimization of the total energy with respect to the atomic coordinates. The dangling bonds of the bottom surface atoms were passivated by pseudohydrogen atoms. Two bottom atomic layers of the slabs were fixed to the ideal positions. Other atoms, including the pseudohydrogen atoms, were relaxed until the remaining forces were less than 20 meV/Å. Pseudohydrogenated slabs were used with the energy cutoff of 250–350 eV. The number of k points in the surface Brillouin zone was 12. The k point sampling was performed by the Monkhorst–Pack scheme [33] with the origin shifted to the Γ point. These parameter values accurately describe

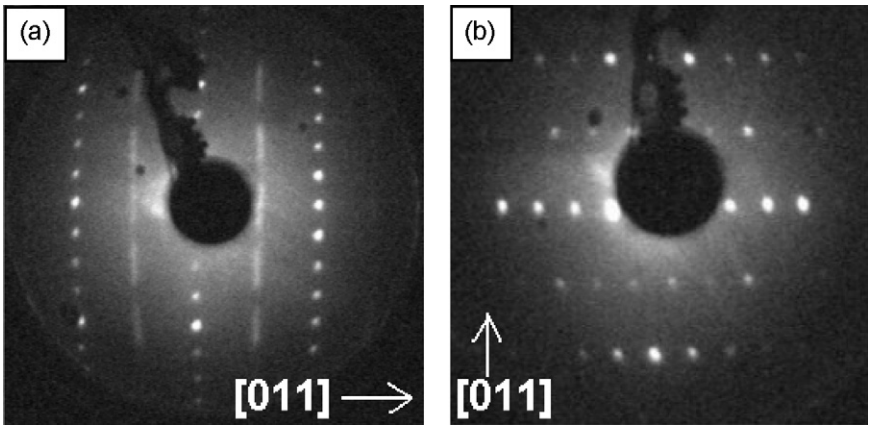

Fig. 2. (a) LEED image from InAs at 55 eV. (b) LEED image from InSb at 44 eV.