The mechanism for the $3 \times 3$ distortion of Sn/Ge(111)

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We show that two distinct $3 \times 3$ ground states, one nonmagnetic, metallic, and distorted, the other magnetic, semimetallic (or insulating) and undistorted, compete in $\alpha$-phase adsorbates on semiconductor (111) surfaces. In Sn/Ge(111), LSDA/GGA calculations indicate, in agreement with experiment, that the distorted metallic ground state prevails. The reason for stability of this state is analysed, and is traced to a sort of bond density wave, specifically a modulation of the antibonding state filling between the adatom and a Ge-Ge bond directly underneath.

I. INTRODUCTION

The study of the so-called $\alpha$-phases (1/3 monolayer adatom coverage) of tetravalent adsorbates on semiconductor surfaces has recently attracted considerable interest, due to the complex and diverse phenomenology displayed by systems that, at a first glance, look very similar, both from a structural and from an electronic point of view. On one side we have Pb/Ge(111) \cite{1,2} and Sn/Ge(111) \cite{4,5,6,7,8}, where a transition from $\sqrt{3} \times \sqrt{3}$ to $3 \times 3$ surface periodicity has been observed below $\sim 200$ K. On the other side, SiC(0001) \cite{12} and K/Si(111):B \cite{13} retain a $\sqrt{3} \times \sqrt{3}$ periodicity at all temperatures, but are insulating, in contrast with simple electron counting rules. All the above systems are characterized, in the $\sqrt{3} \times \sqrt{3}$ phase, by a narrow and half-filled surface band arising from the dangling bond orbital of the adatom. Narrow metallic bands are highly unstable either against electron-electron instabilities (Mott transition), or against genuine structural distortions aimed at lowering the electronic density of states at the Fermi energy \cite{14}. SiC(0001) and, possibly, also K/Si(111):B appear to belong to the former class, due to the large Coulomb repulsion within the dangling bond orbital of the Si adatom. In line with this expectation, SiC(0001) has been recently predicted to be a surface magnetic Mott insulator based on first-principles calculations \cite{15}. Sn/Ge(111) and Pb/Ge(111) belong instead to the class of surfaces where a large structural distortion, leading to a $3 \times 3$ periodicity, removes at least some of the original destabilizing metallic character.

Although considerable progress has been made in the last years, a complete understanding of the physics underlying the appearance of so different phenomena (Mott transition or atomic distortion) at the surface of otherwise very similar systems, is presently missing. In particular, we lack a microscopic understanding of the reasons that make a system decide for one or the other state. This is particularly relevant also in connection with the possibility that these states may be observed at the surfaces of other, presently unexplored, $\alpha$-phases such as Sn/Si(111), Pb/Si(111). Recent work on Sn/Si(111) \cite{17} fails to indicate any sign of transition down to 100 K. Here we focus on Sn/Ge(111), as a prototype of the systems where a large atomic distortion takes place. We investigate the system with first-principles methods, and find that both an undistorted (i.e. structurally $\sqrt{3} \times \sqrt{3}$) but magnetic state, and a $3 \times 3$ structurally distorted state, lower the energy of the originally metallic $\sqrt{3} \times \sqrt{3}$ surface. However, the energy gain is larger for the structurally distorted case, explaining the observed low temperature $3 \times 3$ structure. Moreover, by examining in detail the atomic and electronic structure of the $3 \times 3$ distortion, we are able to highlight the microscopic mechanisms that drive the transition.

II. METHOD

The Sn/Ge(111) surface has been modelled in a repeated supercell geometry where three bilayer slabs of Ge atoms are separated by equivalently thick vacuum regions. Sn adatoms are placed in the T$_4$ position of the upper surfaces while dangling bonds of the lower surfaces are saturated by hydrogen atoms. We performed extensive electronic structure calculations for both the $\sqrt{3} \times \sqrt{3}$ and the $3 \times 3$ surfaces, either in the local (spin) density approximation (LSDA) or including gradient corrections (GC) \cite{18} to the energy functional. Norm-conserving pseudopotential \cite{19} in the Kleinman-Bylander form \cite{20}, a plane-wave basis set with 12 Ry energy cutoff, and a $15 \times 15$ k-points grid to sample the full surface Brillouin zone (SBZ) of the $\sqrt{3} \times \sqrt{3}$ phase were used. For the $3 \times 3$ surface an equivalent SBZ sampling was employed. All systems were structurally relaxed, keeping the bottom Ge-layer and the saturating hydrogen atoms fixed, until the Hellmann-Feynman forces on all other atoms were reduced to less than $\approx 10^{-2}$ eV/a.u.
FIG. 1. Surface band structure of the Sn/Ge(111), calculated in the GC approximation. Left panel: $\sqrt{3} \times \sqrt{3}$ undistorted nonmagnetic surfaces. Middle panel: $3 \times 3$ magnetic surface (here the structural distortion is negligible). Solid line, spin up electrons; dotted lines, spin-down electrons. Right panel: $3 \times 3$ distorted structure (nonmagnetic). In all cases shaded regions represent projected bulk bands.

III. RESULTS

The GC band structure of the unreconstructed Sn/Ge (111) $\sqrt{3} \times \sqrt{3}$ surface are reported on the left panel of Fig. 1. The system is metallic with a single predominant, partially occupied, surface band, originating from adatom dangling bonds, in the bulk projected energy gap. Due to the rather small bandwidth, $w \approx 0.6$ eV, the system presents an instability toward a spin- and charge-density wave of $3 \times 3$ periodicity. The corresponding ground-state band structure is shown in the middle panel of Fig. 1. In agreement with experimental evidence, the magnetically ordered structure is still metallic, although with a reduced density of states at the Fermi energy. A similar result was obtained earlier for the Si/Si(111) surface [21] where, however, the exchange gap was larger and the resulting structure was insulating. The inclusion in the calculation of GC terms to the energy functional turns out to be necessary to stabilize the magnetic structure. This is not surprising as we expect the underlying physics to be rooted in the same aspects (small band width, large coulomb self-interaction) that produce the Mott insulating states in related systems [12,16].

In addition to this magnetic instability metallic Sn/Ge(111) $\sqrt{3} \times \sqrt{3}$ surface is also unstable against a purely structural distortion, where vertical displacements of the adatoms with $3 \times 3$ periodicity, are accompanied by a bond alternation of the underlying substrate. In Fig. 2 the atomic structures of the unreconstructed (left) and reconstructed (right) surface are compared. One of the 3 adatoms rises above the surface while the other two sink deeper in the substrate, the final calculated vertical displacement between the two adatom types being as large as 0.36 Å. The energy gain of the system upon reconstruction is of 9 meV/adatom, to be compared with 1-2 meV/adatom of the magnetic case. The reconstruction is robust with respect to the exchange-correlation scheme used, and LDA and GC give here essentially the same results, indicating that the physics involved is probably well described by a conventional band picture, in spite of the large value of U/W in the surface state band. This point will be addressed later. Our calculated distortion compares favorably with that extracted from very recent x-ray diffraction [11] and also with a previous LDA calculation [8].

The reconstruction develops with no energy barrier: we checked that the energy decreases steadily when the adatom vertical offset is fixed at about 10% of its final value, the substrate atoms being allowed to relax from the unreconstructed positions. In fact, it can be seen from Fig. 2 that the reconstruction pattern involves changes in the (111) bonds-lengths between second and third Ge atomic layers. The reconstruction apparently occurs because the symmetry lowering allows some rehybridization between adatoms, accompanied by a bond alternation in the substrate that stabilizes the deformation.

FIG. 2. Contour plot of the mid-gap state at M point in the SBZ of $\sqrt{3} \times \sqrt{3}$ surface. Full lines enclose regions where the wavefunction is positive; dotted lines enclose negative regions. Note the antibonding character of the wavefunction between the adatom and the substrate. Atomic positions and bonds are also shown for reference.
The mechanism can be better understood by examining the nature of the Wannier function (WF) of the mid-gap state of the $\sqrt{3} \times \sqrt{3}$ surface (approximated here by the wavefunction at the M point, see Fig. 3). The WF originates from the adatom dangling bond but has important contributions from substrate states. In particular it can be seen as an antibonding combination of the adatom dangling bond and the bonding state located in the (111) Ge-Ge bond below it. When the system reconstructs one of the three adatoms becomes inequivalent filling its state completely. By doing so the corresponding (111) Ge-Ge bond is strengthened (due to the bonding character of the WF in that region) while the Sn-Ge one is weakened (the WF is antibonding there); as a result the adatom rises above the surface. The WF’s centered on the other two adatoms are partially depopulated and an opposite relaxation occurs.

To better illustrate this mechanism let us consider a toy system where the relevant structural motif (a Sn adatom and the four Ge atoms underneath) is extracted from the surface and hydrogen atoms are added to saturate Ge dangling bonds. The neutral cluster (Fig. 2, left panel) corresponds to the unreconstructed surface (Fig. 3, left panel) and presents a semioccupied highest molecular orbital (HMO) with antibonding character between Sn and Ge.

When the HMO is completely filled, making the cluster negatively charged, all Sn-Ge bonds weaken and the corresponding distances increase. Not much else happens; in particular the already strong vertical Ge-H bond is not modified significantly. The effect is more dramatic in the opposite situation, when the HMO is emptied making the cluster positively charged (Fig. 2, right panel). As expected from its antibonding character, depopulating the HMO strengthens Sn-Ge bonds shortening their distances, while the lower Ge-H bond is essentially destroyed.

Why does Sn/Ge(111) energetically prefer to distort rather than become Mott-Hubbard insulating? Our results suggest that the $3 \times 3$ distortion is based on the strong antibonding interaction between the adatom dangling bond and the Ge-Ge bond directly underneath. The fact that the energy gain should come by an alternating hybridization/dehybridization of the surface band with a deeper Ge-Ge bond has two implications. The first is that the large value of $U/W$ inside the surface band is not very relevant to this state, unlike the Mott-Hubbard state. The second is that it shows that band-Jahn-Teller, a terminology often used to describe it, is not a correct characterization for this state. It is rather a bond-density-wave. In this case the energy gain does not come from gap-opening, that is only partial, but from the modulation of the strength of the Ge-Ge bonds under the adatoms. Large adatoms, narrow semiconductor gaps and a deformable lattice favor that. These conditions are not met e.g. in SiC(111), where moreover poor screening enhances the value of electron repulsion ($U$).

In conclusion, we have studied the competition between magnetic and distorted nonmagnetic ground states of Sn/Ge(111). Dominance of the latter has been understood as due to a modulation of the antibonding partnership between the adatom and the underlying Ge-Ge bond.

Our calculations were performed on the CINECA Cray-T3E parallel machine in Bologna, using the parallel version of the PWSCF code. Access to the Cray machine has been granted within the Iniziativa Trasversale Calcolo Parallelo of INFM and the initiative Progetti di ricerca di rilevante interesse nazionale of MURST. Sponsorship from INFM/LOTUS and from COFIN97 is also acknowledged.
FIG. 4. Ground state geometric structure of a SnGe$_4$H$_7$ cluster in the neutral (left panel), negatively charged (middle panel) and positively charged (right panel) states. Atomic distances in Å.