ELSEVIER

Surface Science 482–485 (2001) 1350–1354

SURFACE SCIENCE

www.elsevier.nl/locate/susc

Surface geometry and STM image of the Sn/Ge(1 1 1)-3 × 3 reconstruction

L. Jurczyszyn [a,b,*], J. Ortega [a], R. Pérez [a], F. Flores [a]

[a] *Departamento de Física Teórica de la Materia Condensada, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid 28049, Spain*

[b] *Institute of Experimental Physics, University of Wroclaw, pl. Maksa Borna 9, 50–204 Wroclaw, Poland*

Abstract

A theoretical analysis of the STM image of the Sn/Ge(1 1 1)-(3 × 3) surface is presented. In a first step, the atomic structure is reached using a combination of local-orbital and plane-wave density functional methods. We found a ground state geometry presenting two different types of Sn adatoms, with vertical positions differing by ~0.3 Å. In a second step, this geometry was used to analyze the tunneling currents of this surface in a typical STM experiment. In our approach, a Keldysh formalism is used with a coupling between tip and the sample defined by Bardeen-matrix elements: the tunneling currents are found to depend on the semiconductor surface density of states and these Bardeen coupling elements. We study the STM surface corrugation for positive and negative biases and find that both STM images are complementary of each other, in good agreement with the experimental evidence.

Keywords: Surface relaxation and reconstruction; Scanning electron microscopy (SEM); Tunneling; Germanium; Tin

1. Introduction

A one-third of a monolayer of Sn atoms on Ge(1 1 1) displays a puzzling transition at around 50 K, with a reversible change from the $(\sqrt{3} \times \sqrt{3})$ pattern to a 3 × 3 periodicity when the temperature is lowered [1,2]. The 3 × 3 atomic structure has been analyzed using a combination of local-orbital and plane-wave density functional methods [3,4], the results showing that the ground state geometry presents two different types of Sn adatoms whose vertical positions differ by ~0.3 Å.

Fig. 1 shows this 3 × 3 geometry, with the atom Sn1 displaced upwards by ~0.18 Å and the atoms Sn2 displaced downwards by ~0.08 Å. Details of the ground state geometry, showing the displacements of the semiconductor last layer atoms are given in Ref. [4].

The STM data of Refs. [1,2] show that the positive and negative bias images of the Sn/Ge(1 1 1)-(3 × 3) reconstruction were complementary, in such a way that for currents taken with electrons tunneling into the tip, the Sn adatom appeared as displaced upwards (in agreement with the ground state geometry), while in the image taken with a reverse bias, the apparent surface

* Corresponding author. Address: Institute of Experimental Physics, University of Wroclaw, pl. Maksa Borna 9, 50–204 Wroclaw, Poland. Fax: +48-71-328-73-65.

E-mail address: lju@alpha.ifd.uni.wroc.pl (L. Jurczyszyn).

0039-6028/01/$ - see front matter
PII: S0039-6028(01)00711-7

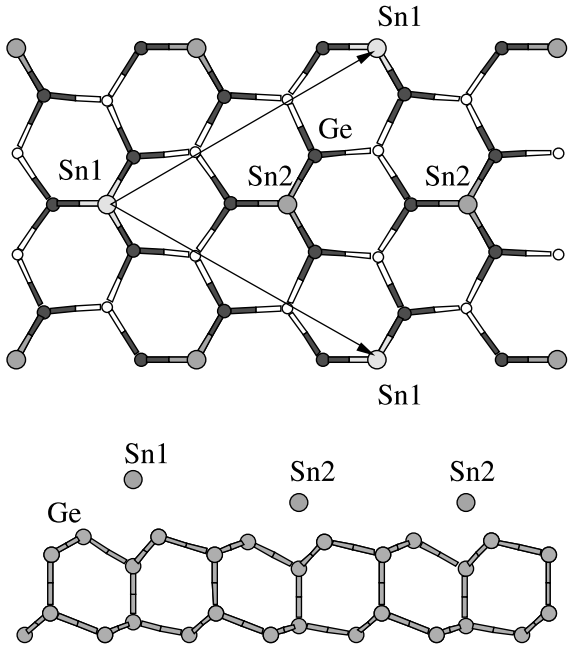

Fig. 1. Atomic geometry of the Sn/Ge(1 1 1)-(3 × 3) surface.

geometry was the complementary (with the Sn atom moving downwards). Although this effect was expected to be related to the local density of states associated with adatoms Sn1 and Sn2, no calculation has yet supported this point of view.

Fig. 2a shows the 3 × 3-surface bands calculated using the LDA code. As explained in Refs. [3,4], the lowest band is associated with the Sn1 adatom of Fig. 1 and the two upper bands with the two Sn2 adatoms of the 3 × 3 reconstruction. Fig. 2b also shows the local density of states associated with Sn1 and Sn2 atoms. The two peaks around the Fermi level correspond to the lower and upper bands of Fig. 2a. We should say that the lower band (and lower peak in Fig. 2a) is filled with two electrons, while the two upper bands are filled by only one electron. Notice that this charge transfer stabilized the surface and is associated with the surface geometry presented in Fig. 1.

The crucial question we address in this paper is the following: can the DOS associated with the surface bands explain the complementarity of the STM images taken for positive and negative biases?

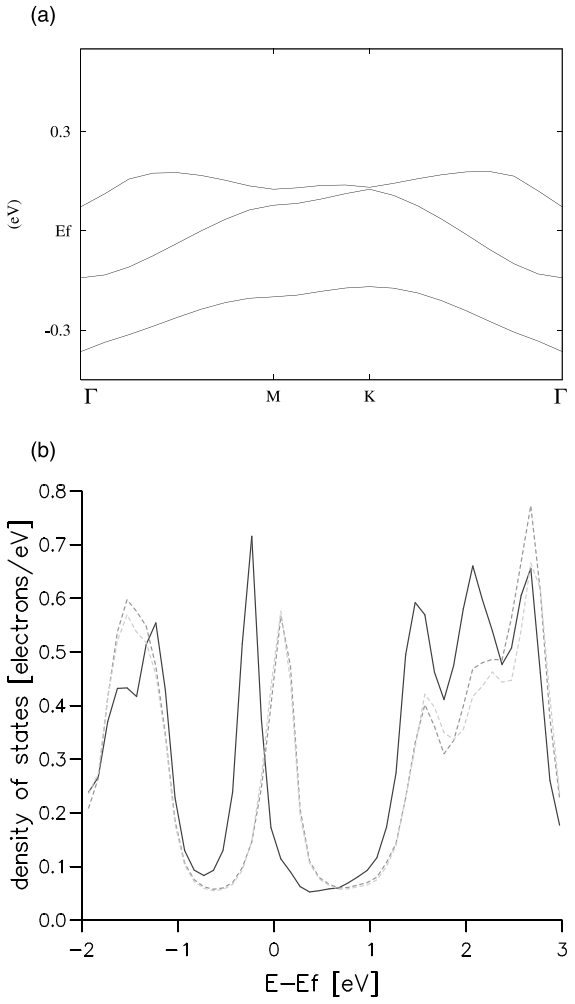

Fig. 2. Electronic structure of Sn/Ge(1 1 1)-(3 × 3) surface: (a) surface band structure obtained from LDA calculations with three bands corresponding to the dangling bonds of the Sn1 and the Sn2 atoms from Fig. 1, (b) local density-of-states distributions at the topmost Sn1 adatom (solid line) and two Sn2 adatoms displaced downwards (dashed lines).

2. Tunneling current

The analysis of the tunneling current between the tip and the substrate is based on a LCAO method that describes the system by the following Hamiltonian:

$$\hat{H} = \hat{H}_{\mathrm{T}} + \hat{H}_{\mathrm{S}} + \hat{H}_{\mathrm{I}}, \tag{1}$$

where the tip (T) and the sample (S) are described independently, and the coupling is given by $\hat{H}_I$ (see Ref. [5] for further details). Assuming $\hat{H}$ to be known, the tunneling current to all orders in tip–sample coupling, is given by:

$$J = (4e\pi/\mathrm{i}\hbar) \times \int_{-\infty}^{+\infty} \mathrm{Tr}[\hat{T}_{TS}\hat{\delta}_{SS}(\omega)\hat{D}^R_{SS}(\omega)\hat{T}_{ST}\hat{\delta}_{TT}(\omega)\hat{D}^A_{TT}(\omega)] \times [f_T(\omega) - f_S(\omega)]\,\mathrm{d}\omega \quad (2)$$

where $(\hat{D}^R_{SS}(\omega))$ and $(\hat{D}^A_{TT}(\omega))$ are given by:

$$\hat{D}^R_{SS}(\omega) = [\hat{I} - \hat{T}_{ST}\hat{g}^R_{TT}(\omega)\hat{T}_{TS}\hat{g}^R_{SS}(\omega)]^{-1} \quad (3)$$

and

$$\hat{D}^A_{TT}(\omega) = [\hat{I} - \hat{T}_{TS}\hat{g}^A_{SS}(\omega)\hat{T}_{ST}\hat{g}^A_{TT}(\omega)]^{-1} \quad (4)$$

In Eq. (2) $\hat{\delta}_{SS}$ and $\hat{\delta}_{TT}$ are the density matrices associated with the sample and the tip respectively; while $\hat{T}_{TS}$ is the hopping matrix defining the tip–sample interaction. On the other hand, $f_T(\omega)$ and $f_S(\omega)$ define the tip and sample Fermi distribution functions. For zero temperature and a bias V, Eq. (2) reads as follows:

$$J = (4\pi e^2 V/\hbar) \times \int_0^{eV} \mathrm{Tr}[\hat{T}_{TS}\hat{\delta}_{SS}(\omega)\hat{D}^R_{SS}(\omega)\hat{T}_{ST}\hat{\delta}_{TT}(\omega)\hat{D}^A_{TT}(\omega)]\,\mathrm{d}\omega \quad (5)$$

The quantities defining J are the tip and sample density matrices, and the tip–sample coupling $\hat{T}_{TS}$.

$\hat{\delta}_{SS}$ has been obtained from the LDA results calculated using the local basis of a Fireball code. From the calculation of the Sn/Ge(1 1 1)-3 × 3 reconstruction we obtain the sample Hamiltonian in a nonorthogonal basis; as Eq. (3) is expressed in a orthogonal basis, we have to convert this basis into an orthogonal one by means of the transformation:

$$\hat{H}_{\mathrm{orthogonal}} = \hat{S}^{-1/2}\hat{H}_{\mathrm{nonorthogonal}}\hat{S}^{-1/2} \quad (6)$$

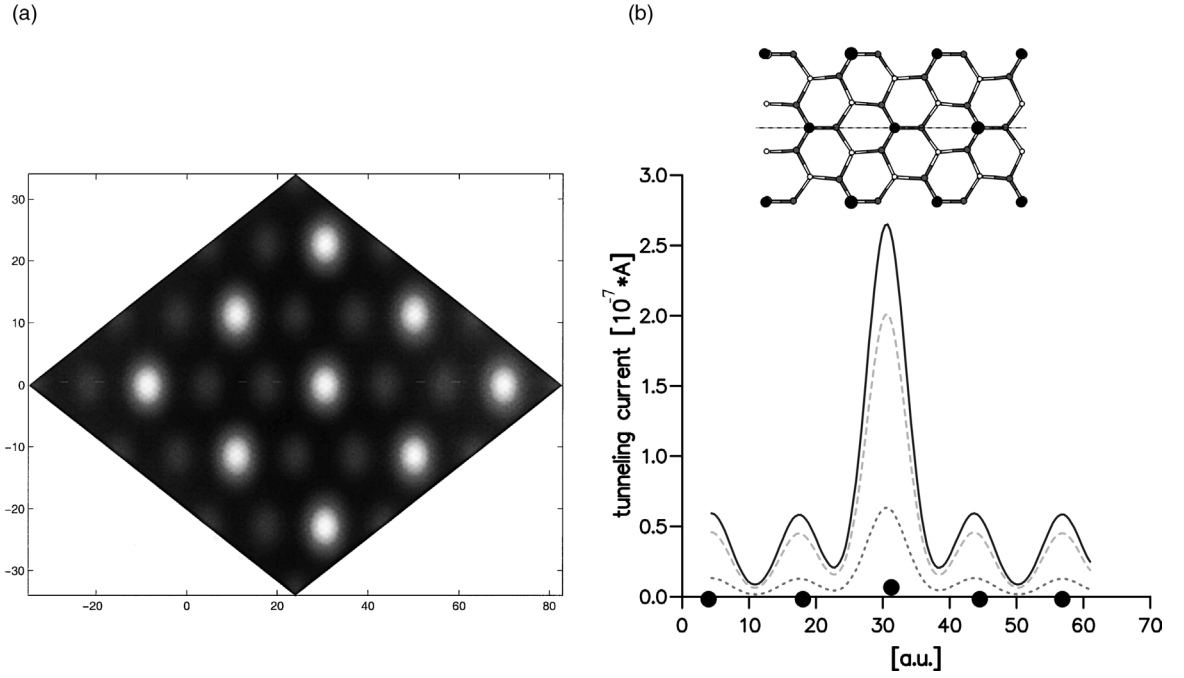

Fig. 3. (a) STM image of the occupied states at Sn/Ge(1 1 1)-(3 × 3) surface simulated in constant-height mode. Coordinates are given in a.u. and (b) STM profile along the line passing above Sn adatoms. Calculations have been performed for bias −0.55 V and tip–sample distance 5.12 Å.

where $\hat{S}$ is the overlap matrix associated with the nonorthogonal Fireball local-orbitals.

The description of the electronic structure of the tip was performed with the help of the cluster–Bethe-lattice method [6]. In this model the tip is represented by a five atom pyramidal cluster (with a single atom at the cluster apex), and the influence of the rest of the tip is simulated by the Bethe lattice connected to this cluster. Self-consistency has been introduced in the cluster by imposing a local charge neutrality condition at each atom.

Finally, the hopping interactions $\hat{T}_{\mathrm{TS}}$ have been calculated using the expression for the Bardeen current tunneling between particular orbitals:

$$T_{i,j} = -(0.5\gamma)\int_{\delta_{ij}} (\psi_i \nabla\psi_j - \psi_j \nabla\psi_i)\,\mathrm{d}\mathbf{s} \qquad (7)$$

where γ is a coefficient that typically takes values in the range 1.3–1.5 [7].

3. STM simulations and conclusions

The theoretical study presented here is based on the simulation of the STM process of Sn/Ge(1 1 1)-(3×3) substrate in constant-height mode. Calculations of the STM images have been performed for the tungsten tip located 4.25 and 5.12 Å above the topmost Sn adatoms; these distances have been adjusted to give the same maximum current for positive and negative biases. Figs. 3 and 4 present the simulated images of filled and empty states received with biases -0.55 and 0.55 V respectively, together with the STM profiles taken along the line passing directly above Sn adatoms.

These results clearly confirm the effect observed in STM measurements [1,2]. The images of filled and empty states present opposite tendency: for filled states the dominating features are located at the topmost Sn1 adatoms (Fig. 3), while in the image created by unoccupied states these features

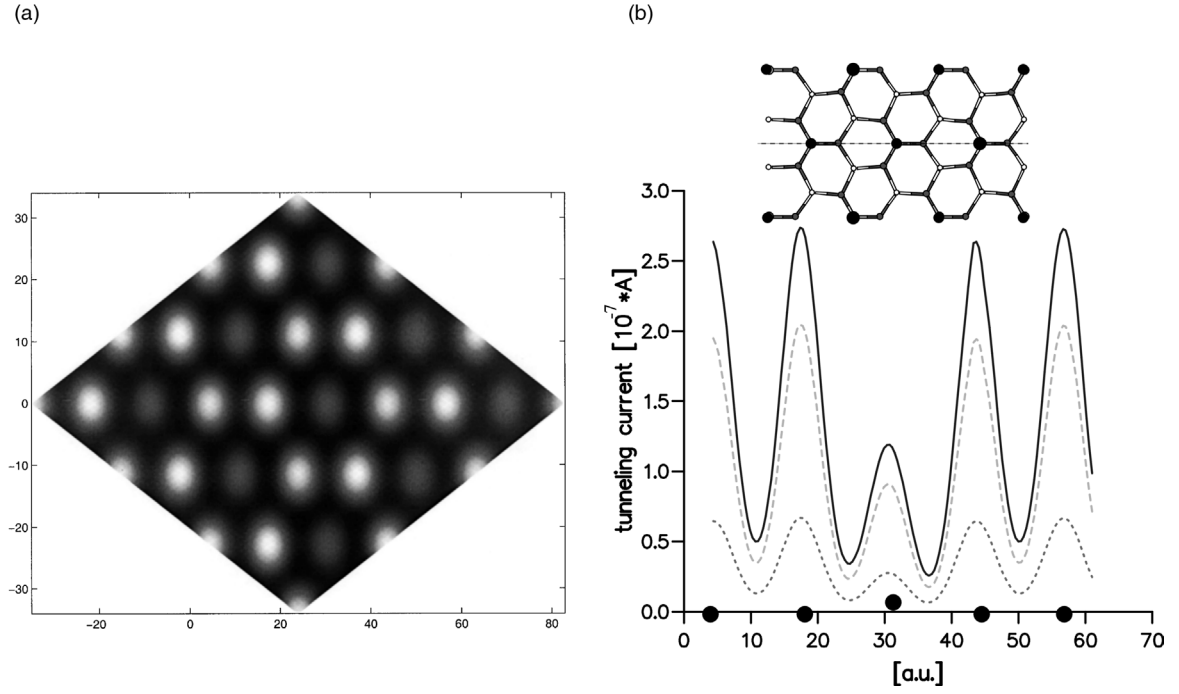

Fig. 4. (a) STM image of the unoccupied states at Sn/Ge(1 1 1)-(3×3) surface simulated in constant-height mode. Coordinates are given in a.u. and (b) STM profile along the line passing above Sn adatoms. Calculations have been performed for bias 0.55 V and tip–sample distance 4.25 Å.

appear at the Sn2 atoms shifted downwards (Fig. 4). This result is a direct consequence of electronic structure of the Sn/Ge(1 1 1)-(3 × 3) presented in Fig. 2. For negative bias the tunneling takes place from occupied states, which are localized at Sn adatoms shifted upwards (see Fig. 2), and therefore dominating protrusions appear also above these topmost adsorbates. For the tunneling through unoccupied states of the substrate (positive bias) the situation is opposite: empty states are localized at the Sn adatoms shifted downwards, and therefore the features connected with these Sn adatoms dominate in STM image.

The STM profiles in Figs. 3 and 4 present also the evolution of the current components connected with the tunneling through s and p_z orbitals of the atoms from the substrate (dotted and dashed lines respectively). They show that in both cases the protrusions corresponding to the Sn atoms are built up mainly by p_z-components (p_z is oriented perpendicular to the surface) while the contribution coming from s orbitals of the substrate atoms is much weaker with negligible p_{xy} contributions.

In conclusion our theoretical results are in good agreement with the experimental STM image and give further support to the (3 × 3) geometry presented in Ref. [4].

Acknowledgements

One of us (L.J.) thanks the Spanish Ministerio de Education y Cultura for financial support. This work was funded by the Spanish CICYT under contract no. PB99-0028.

References

[1] J.M. Carpinelli, H.H. Weitering, E.W. Plummer, R. Stumpf, Nature 381 (1996) 398.
[2] J.M. Carpinelli, H.H. Weitering, M. Bartkowiak, R. Stumpf, E.W. Plummer, Phys. Rev. Lett. 79 (1997) 2859.
[3] J. Avila, A. Mascaraque, E.G. Michel, M.C. Asensio, G. LeLay, J. Ortega, R. Perez, F. Flores, Phys. Rev. Lett. 82 (1999) 442.
[4] J. Ortega, R. Perez, F. Flores, J. Phys.: Condens. Matter B 12 (2000) L21.
[5] N. Mingo, L. Jurczyszyn, F.J. Garcia-Vidal, R. Saiz- Pardo, P.L. de Andres, F. Flores, S.Y. Wu, W. More, Phys. Rev. B 54 (1996) 2225.
[6] L. Martin-Moreno, J.A. Verges, Phys. Rev. B 42 (1990) 7193.
[7] F. Flores, A. Martin-Rodero, E.C. Goldberg, J.C. Duran, Nuovo Cimento D 10 (1988) 303.