

***Ab initio* study of height contrast in scanning tunneling microscopy of Ge/Si surface layers grown on Si(111) in presence of Bi**

Ruslan Zhachuk^{1,2,*} and José Coutinho²

¹*Institute of Semiconductor Physics, pr. Lavrentyeva 13, Novosibirsk 630090, Russia*

²*13N, Department of Physics, University of Aveiro, Campus Santiago, P-3810-193 Aveiro, Portugal*

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It has been recently demonstrated that Bi surfactants over Ge layers grown on Si(111) allow us to distinguish Ge and Si covered regions through a scanning tunneling microscope. We revised this problem by considering geometric (or structural) and electronic effects to explain the measured apparent height difference of relaxed surface layers. The local density of states and related decay lengths into vacuum are calculated within density functional theory for each surface of interest. The results are compared with recent experimental data from a scanning tunneling spectroscopy study [J. Mysliveček, F. Dvořák, A. Strážek, and B. Voigtländer, *Phys. Rev. B* **81**, 245427 (2010)].

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The usage of surfactants provides an effective route to modify surface properties in a way to promote growth of relatively thick epitaxial layers of Ge on Si(111) substrates. Their role is twofold: by *floating* on top of growing layers, they suppress both the intermixing of Si and Ge chemical species, and the formation of multilayered islands. Although As and Sb surfactants soon became popular,¹ it has been realized more recently that Bi performs even better. In particular, by using Bi as a terminating layer on a Ge/Si(111) surface, it is possible to distinguish between Si and Ge layers through a scanning tunneling microscope (STM).² This valuable property paved the way for the successful production of self-assembled Ge/Si nanostructures in a controlled manner.²⁻⁴ It also allowed scientists to study Ge/Si intermixing in surface layers at the atomic scale,⁵ and the observed height contrast helped them to understand the nature of the symmetry breaking during the growth of two-dimensional Ge islands on Si(111) by using a marker technique.⁶

We can evoke several reasons to explain the observed height contrast, and these may be of a structural or electronic nature. A structural reasoning is based on the larger lattice constant of Ge compared to Si, which could cause a vertical lattice distortion in order to relieve the built-in strain. However, the measured height difference of up to 1.0 Å is at least one order of magnitude larger than that obtained from simple elasticity theory. Alternatively, the observed height contrast could arise from different Bi-induced reconstructions on Ge(111) and Si(111) surface layers. Again, we have to rule this out since Bi (and Sb) atoms were observed to form the same $\sqrt{3} \times \sqrt{3}$ -periodic trimer arrangements on both Si and Ge surfaces.^{2,7,8} Thus, the answer for the observed height contrast is most likely to arrive from electronic arguments. To this end, Miwa *et al.*⁹ carried out a density functional theoretical (DFT) study, from which a 0.1 Å geometric height difference between the top Si and Ge layers was reported. Although they found (i) a different local density of states on Bi trimers over Si and Ge related areas, (ii) a valence band shift across the Ge/Si(111)-Si/Si(111) interface, and (iii) no relevant differences in the positioning and character of the lowest unoccupied states of Ge and Si surface areas, it was not clear how these features could be connected to the contrasting images.

Recently, Mysliveček *et al.*¹⁰ performed a detailed low temperature scanning tunneling spectroscopy (STS) study of the Ge/Si(111) system. The experiments show that the height contrast from empty electronic states is considerably stronger than that from filled states, and therefore at variance with the calculations.⁹ Further, the height difference in filled states was observed to be almost independent of the applied voltage.

Since STM is intrinsically and solely sensitive to the electronic density of states, it does not have access to the actual geometric height difference between individual atom nuclei of Ge/Si surface layers. Moreover, relevant electronic states lie within a few eV from the surface Fermi level, where large dispersion effects due to delocalization and hybridization hinder the identification of energy levels with specific atomic sites, thus making the STS reports problematic and rare.^{11,12} Since *ab initio* modeling may play a complementary and key role in surmounting some of these difficulties, we report on local density of states (LDOS) calculations and LDOS decay length into vacuum of Sb- and Bi-covered Si and Ge layers, aiming at establishing a link between the surface electronic structure and the observed height contrast.

The calculations were carried out self-consistently from first principles by using the local density functional SIESTA code.¹³ The exchange-correlation functional is that of Ceperley-Alder as parametrized by Perdew and Zunger.¹⁴ Norm-conserving pseudopotentials were employed to account for core states,¹⁵ whereas valence states are spanned on linear combinations of numerical atomic orbitals of the Sankey-Niklewski type, generalized to be arbitrarily complete with the inclusion of multiple ζ orbitals and polarization states.¹³ In the present calculations, polarized double- ζ functions were assigned for all species. This means two sets of *s* and *p* orbitals plus one set of *d* orbitals on Si, Ge, Sb, and Bi atoms, and two sets of *s* orbitals plus a set of *p* orbitals on H. In order to assess the convergence of LDOS decay length calculations, we filled some vacuum space with a grid of *ghost* atoms with a basis similar to that of Si atoms. The charge density, potential terms, and LDOS were calculated on a real space grid with an equivalent cutoff of 200 Ry. Further details, including convergence tests may be found elsewhere.¹⁶

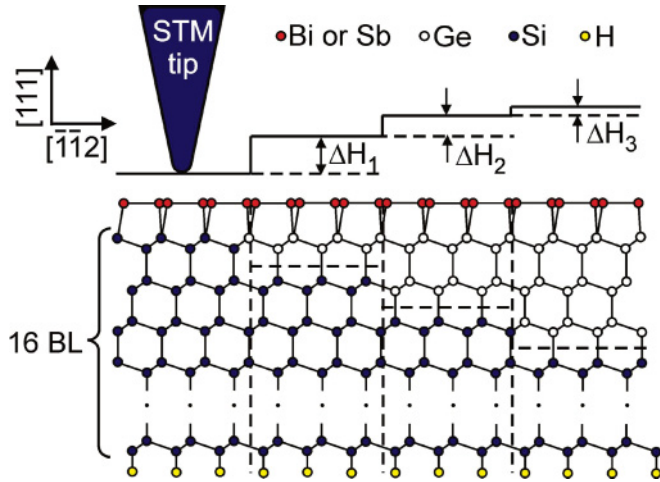


FIG. 1. (Color online) Structural model slabs used in calculations. ΔH_1 , ΔH_2 , and ΔH_3 represent apparent height differences between adjacent regions with different numbers of Ge layers. The stepwise line hovering the surface represents the trajectory of an STM tip.

In order to study the apparent height contrast between surface regions containing different numbers of Ge layers (see Fig. 1), slabs with up to three Ge layers and a specific surfactant on top (Bi or Sb) were considered. Slabs were made of 16 atomic Ge/Si bilayers (BLs), separated by an 18 Å thick vacuum layer. The $\sqrt{3} \times \sqrt{3}$ reconstruction containing Bi (Sb) trimers on top of T_4 sites of the (111) surface was used to fulfill the periodic boundary conditions along the lateral directions.^{7,8} All Si dangling bonds at the unreconstructed bottom surface were saturated by hydrogen atoms. For such supercells, an $8 \times 8 \times 1$ \mathbf{k} -point grid was found adequate in providing convergence in sampling the Brillouin zone.¹⁷ For bulk Si calculations we used a similar supercell (with equilibrium lattice constant $a_0 = 5.420$ Å), consisting of 15 Si BLs and an $8 \times 8 \times 2$ \mathbf{k} -point sampling grid. On slab calculations, the geometric positions of all atoms from the top 15 Ge/Si BLs plus Bi/Sb trimers were allowed to relax, while the bottom Si-H units are kept frozen. The geometry was optimized until all atomic forces became less than 0.01 eV/Å.

It is important to align the energy scale of LDOS results from different slabs. This was carried out shifting the Kohn-Sham spectrum by the difference of the average electrostatic potential from bulklike slab layers to the similar value found from a bulk (vacuum free) calculation.¹⁸ The resulting energy shifts were of the order of 0.02 to 0.06 eV. The Fermi energy was then set to the midgap energy from a bulk calculation, and this was considered the origin of the energy scale.

As suggested in Ref. 10, in a low voltage regime $-3.0 < U < +3.0$ V, the main electronic contributions to the apparent height contrast are from surface LDOS and from the local tunneling barrier height, which can be described in terms of a decay length λ . According to Ref. 19, in this voltage regime the tunneling current I through a tip apex at a height h above the surface can be written as

$$I \propto \exp\left(-\frac{2h}{\lambda}\right) \int_{E_F}^{E_F \pm eU} v(E) dE, \quad (1)$$

where v is the surface LDOS and the integration is carried out on an energy window eU below or above E_F depending on the bias of the applied voltage. Equation (1) neglects the tip shape, its density of states, and transport properties, and assumes that the LDOS dependence on the height and energy can be separated into the exponential prefactor and integrand terms, respectively. In practice, LDOS as calculated from the DFT Kohn-Sham states already captures both energy and height dependence.

Electronic LDOS was calculated on a grid of points across the whole supercell volume on a set of energies with a step of 0.2 eV. This was then integrated over a 5.0 Å thick layer centered on the surfactant atomic layer. The calculated LDOS spectra depended weakly on the exact positioning of the integration layer (provided that it includes the surfactant atoms). Unlike more sophisticated calculations,²⁰ the LDOS reported here was not taken at the height of a STM tip which would be 8 to 12 Å above the Bi atoms.¹⁰ On the other hand, the method adopted has been widely employed and usually shows good qualitative agreement with the experiments.^{16,21,22} STS test calculations were carried out by LDOS integration over a layer containing the Si dimers on Si(100)- 2×1 and As adatoms on As/Si(111) systems. Our results show excellent agreement with results reported in Refs. 11 and 23 where the data was obtained at realistic tip heights. Our calculations approximately correspond to STS spectra with low spatial resolution acquired with a dull tip. The calculated LDOS spectra for Si- and Ge-related $\sqrt{3} \times \sqrt{3}$ -Bi slabs are depicted in Fig. 2(a). These should be compared to the experimental STS data in Fig. 2(c), reproduced from Fig. 3(a) in Ref. 10. If we ignore some small differences discussed ahead, we conclude that the experimental and theoretical spectra are very similar, especially if we take into account that a single tungsten tip and a heavily As doped Si(111) substrate were used in the measurements [see the Fermi level position in

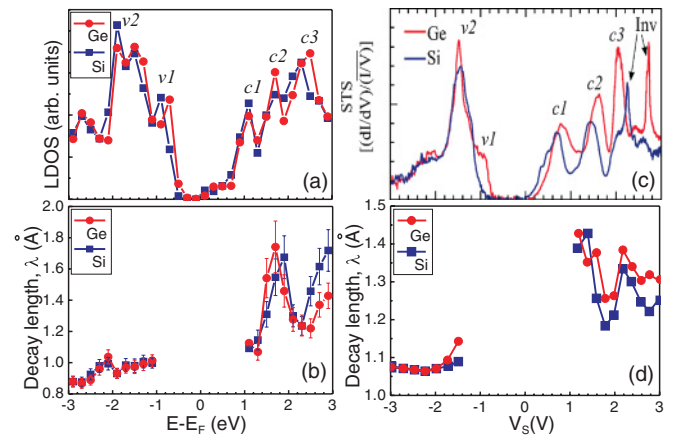


FIG. 2. (Color online) (a) Calculated LDOS spectra for Si- and Ge-related $\sqrt{3} \times \sqrt{3}$ -Bi slabs. Valence band (v_1 and v_2) and conduction band (c_1 to c_3) LDOS features are labeled according to Ref. 10. (b) Decay lengths λ of the LDOS into vacuum along with error bars from the fitting procedure (see text). (c) Experimental STS spectra of Si- and Ge-related $\sqrt{3} \times \sqrt{3}$ -Bi surfaces [reproduced from Fig. 3(a) in Ref. 10]. (d) Decay lengths of the tunneling current measured for the surfaces from (c) (taken from the data shown in Fig. 6 of Ref. 10).

Fig. 2(c)].¹⁰ In fact, this similarity further supports the adopted Bi reconstruction geometry (known as the *milkstool* model⁷), where a one monolayer (ML) saturated layer of Bi atoms form a $\sqrt{3} \times \sqrt{3}$ trimer reconstruction. The LDOS spectra calculated for the $\alpha\text{-}\sqrt{3} \times \sqrt{3}$ model with a $1/3$ ML saturation coverage⁷ shows a totally different shape and will not be considered further.

The two narrow peaks labeled as Inv in the STS spectra of Fig. 2(c) arise from the onset of the bulk inversion caused by the tip-induced band bending.¹⁰ The blue shift of the Ge-related part of STS spectra in the conduction band is probably due to a different screening of the tip electrical field at Si and Ge surface areas.¹⁰ These observations indicate that the STS curves include also non-density-of-states features. Their reproducibility is beyond the applicability of the present calculations. Further, when comparing spectra from Figs. 2(a) and 2(c), one should also mind that the calculated LDOS is based on local density Kohn-Sham eigenvalues with well known insufficiencies, especially regarding the underestimation of unoccupied level energies. This could be improved with a better treatment of exchange and correlation interactions for excitations. The experimental STS data in Fig. 2(c) suffer from electron-transport problems due to low measurement temperatures. The latter effects include broadening of the surface band gap in STS and shifting of peaks in STS to higher energies.¹⁰

Figure 2(a) exhibits all LDOS related features resolved in Fig. 2(c), namely, v_1 and v_2 valence band peaks, and c_1 , c_2 , and c_3 peaks in the conduction band. The calculated blue shift of the highest occupied LDOS in Ge-related areas [see Fig. 2(a)] is in line with the STS spectral shoulder v_1 , as well as with previous calculations.⁹ As it was mentioned previously, the strong contrast effects must arise from empty band states, and here no significant differences were found between Ge- and Si-related spectra, with the exception of the LDOS shape around the c_2 peak. Other apparent feature differences are beyond the accuracy of the calculations. The enhancement of the c_2 peak with the inclusion of one Ge bilayer might be the reason of the increased height contrast between Ge and Si surface areas when using Bi. Inspection of the one-electron states in the region of c_2 was not clarifying with regard to the origin of this effect. It is important to note that in the case of using Sb surfactant, the LDOS spectra of empty states from Ge- and Si-related slabs were essentially similar. This finding is in agreement with the absence of Ge/Si height contrast in experimental STM images when using Sb as surfactant.²

Figure 2(b) shows the calculated decay length of the LDOS into vacuum. This was obtained from an analysis of exponential tails from the LDOS(E, z) averaged over xy planes and plotted along z . Large error bars for conduction band states indicate a considerable departure from the exponential shape. The figure clearly shows that states around 1.8 eV are the most diffuse and dragged out into vacuum. This energy corresponds to the region of the c_2 peak, and it is in agreement with the decay length measurements shown in Fig. 2(d). From this result we infer that surface states contributing to the c_2 peak have a prominent impact on the resulting STM contrast effect.

No noticeable differences were found in the LDOS spectra and decay lengths from valence states of Si and Ge-related surfaces. This accounts well for the STS measurements, and

underpins the conduction band origin of the apparent height difference. Hence, at negative bias the observed height contrast is mostly due to a geometric height difference between Ge and Si surface layers. Indeed, for a single Ge BL the geometric height of Bi surfactant atoms is 0.22 Å above those covering a Ge-free Si(111) surface. This figure compares well with the experimentally measured values of about 0.2 to 0.3 Å, as well as with the nearly insensitivity of this measurement to the applied voltage for negative bias.¹⁰ The corresponding geometric height difference when using Sb as a surfactant is 0.190 Å.

We inspected the origin of the individual LDOS peaks in Fig. 2(a), and for this purpose the LDOS was integrated in spheres of 1.0 Å radii. This procedure is equivalent to using a sharper STS tip, so that the space-resolved LDOS data can now unravel features originating from different surface areas. Several locations were chosen for placing the integration sphere, specifically (i) the center of the triangle formed by three closest Bi trimers; (ii) 1.0 Å above a Bi atom, and (iii) 1.0 Å above the center of a Bi trimer. When the LDOS is integrated in location (i), the most prominent peaks are c_1 and the left part of v_2 . The right part of v_2 dominates when the LDOS is integrated in location (ii). Therefore, the v_2 peak as shown in Fig. 2(a) is not split; instead, it consists of two peaks originating in different surface areas separated by about 4 Å. Since area (i) is about 1 Å below area (ii), its relative contribution to the STS spectra could be low. This would explain why STS spectra in Fig. 2(c) show a single v_2 peak.

It is known that depending on the applied voltage, the $\sqrt{3} \times \sqrt{3}$ -Bi reconstruction appears in a STM either like a honeycomb pattern or as bright Bi trimers,⁷ much like positive/negative images. Figure 3 shows a section of the LDOS spectra near the c_1 peak for a Si(111) slab. For each data point there is a corresponding simulated STM image below, showing that there is an evident correlation between c_1 and the STM pattern change from honeycomblike (left) to bright Bi trimers (right) when increasing the voltage. This observation is clearly in line with the prominence of the c_1 peak when the LDOS is integrated at the location (i). This is so because

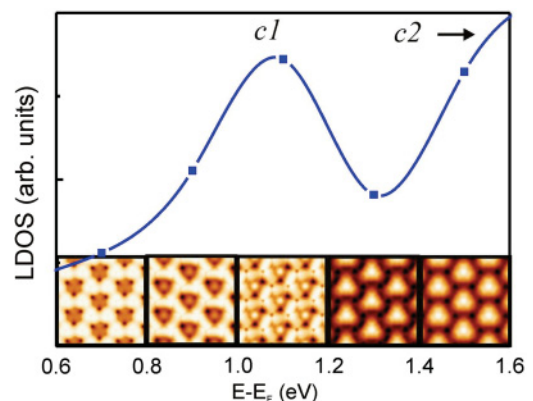


FIG. 3. (Color online) Part of the LDOS spectra with data points (squares) and corresponding simulated STM images. The solid line is provided for eye guidance purposes. Calculated STM images $20 \times 20 \text{ \AA}^2$ were produced by using the WSXM code,²⁴ within the Tersoff-Hamann approximation assuming a constant current STM operation mode.²⁵

these sites are located at regions of the honeycomb shapes with maximum LDOS intensity.

When the LDOS is integrated in location (iii), i.e., above a Bi trimer, the c_2 peak becomes the most intense in the spectrum, and its amplitude is higher for Ge- than for Si-related slabs. This indicates that the empty electronic states which enhance the height contrast are mostly localized over the Bi trimers. Since these states protrude into vacuum, they cause the pronounced decay length peak in Fig. 2(b) at around 1.8 eV.

STM experiments show that deeper surface layers of Ge (second and third layers) also contribute to the apparent height contrast in STM as depicted in Fig. 1.²⁶ We calculated the LDOS spectra on slabs with up to three layers of Ge atoms, and no contributions other than purely geometric were found. That is, the LDOS spectra and decay lengths remain the same as those obtained from slabs with a single Ge layer. The calculated geometric height differences (following the notation in Fig. 1) are $\Delta H_1 = 0.219 \text{ \AA}$, $\Delta H_2 = 0.123 \text{ \AA}$, and $\Delta H_3 = 0.115 \text{ \AA}$.

In conclusion, the nature of the apparent height contrast in Ge/Si surface layers in a STM when using Bi as surfactant

was investigated theoretically from the LDOS using density functional theory. We show that when STM probes filled electronic states (negative bias), the observed height contrast is mostly due to the geometric height difference of surface layers. Conversely, in empty electronic states (positive bias) the c_2 peak of the LDOS from slabs with a Ge sublayer is enhanced. The related electronic states are localized above Bi trimers and correspond to large (1.6–1.8 Å) exponential decay lengths. This effect was not found when using Sb as the surfactant in agreement with experiments. Additional Ge layers were found to have a purely geometric contribution to the STM height contrast. Finally, we found that electronic states shouldering the c_1 peak account for the STM pattern change from honeycomb to bright Bi trimers when increasing voltage.

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*zhachuk@gmail.com

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