Pis'ma v ZhETF, vol. 96, iss. 1, pp. 33 – 36 © 2012 July 10

Ab initio electronic structure of Ge(111)-(2×1) surface in the presence of surface vacancy. Apllication to STM data analysis

S. V. Savinov[1)], *A. I. Oreshkin, S. I. Oreshkin**

Department of Physics, Lomonosov Moscow State University, 119991 Moscow, Russia

**Sternberg Astronomical Institute, Lomonosov Moscow State University, 119991 Moscow, Russia*

Submitted 26 May 2012

We present the results of first principles modeling of Ge(111)-(2×1) surface in the presence of atomic vacancy in surface bi-layer. We showed that simple crystal structure defect affects surface electronic structure to the extent comparable with the influence of doping atom. We demonstrated the strong difference of surface LDOS structure above surface defects of different kind. We have proved that spatial oscillations of LDOS exist around individual surface vacancy in the same tunneling bias range as in case of donor doping atom on Ge(111)-(2×1) surface.

Introduction. Electronic properties of solid body surface for a long time attract researches attention. Partially this is caused by the successes of modern microelectronics industry. Devices produced by vacuum UV lithography 28-nm technology are already in the bulk production. The width of insulating layers is comparable with the Bohr radius of outer electronic shell for shallow impurities (of order of 100 Å). Thus single atomic defect in principle can change *macroscopic* properties of the whole microelectronic structure. The industry faces the lack of information on local electronic properties.

Below we report on the results of *ab initio* numerical modeling of Ge(111) surface's with (2×1) reconstruction electronic properties in the presence of atomic vacancy in surface reconstruction bi-layer. We have performed our first principles calculations by means of DFT method in LDA approximation as implemented in SIESTA [1] package. Some details can be found in [2]. The use of strictly localized numeric atomic orbitals is necessary to be able to perform modeling of large surface cell. In present work surface slab is composed from 7×21 cells of elementary 2×1 reconstruction, each 8 Ge atomic layers thick (total 2645 atoms). The vacuum gap between neighboring slabs in z direction is approximately 20 Å. The dangling bonds of Ge atoms at the slab's bottom surface are terminated with H atoms to prevent surface states formation. One Ge atom is removed from top surface bi-layer at the slab center. The geometry of the structure was fully relaxed until interatomic forces have became less then 0.01 eV/Å. As the last step the spatial distribution of Khon–Sham wavefunctions and surface LDOS were calculated.

Surface local density of states. We would like to stress the fact, that with STM we are measuring LDOS *above* the surface (strictly speaking – tails of LDOS), and as such, in our DFT calculations we are interested in the following quantity:

$$LDOS(\mathbf{r}_{x,y}, \mathrm{eV}) = \sum |\Psi(\mathbf{r}_{x,y})|^2 \,\tilde{\delta}(E - E_i)|_{z=\mathrm{const}},$$

where Ψ are Khon–Sham eigenfunctions, $\tilde{\delta}$ is non-zero width smearing function, E_i are Khon-Sham eigenvalues, and summing is evaluated at certain plane, located a few angstroms above the surface, at certain tunneling bias voltage.

This way we can calculate and plot scalar field of surface $\mathrm{LDOS}(x, y, \mathrm{eV})$ in space-energy coordinates (Fig. 1c). To be absolutely clear, in the text below by LDOS we denote the *surface LDOS* as measured by STM. In Fig. 1 LDOS is shown as the surface of constant value colored by applied bias. Areas with high values of LDOS are located inside volume confined by aforementioned surface. LDOS is shown above only single π-bonded row to make clear impression of the LDOS local structure. There exists substantial difference in behavior between $\mathrm{LDOS}(x, y, \mathrm{eV})$ and integrated $\mathrm{STM}(x,\, y,\, \mathrm{eV}) = \int_{E_\mathrm{F}-\mathrm{eV}}^{E_\mathrm{F}} \mathrm{LDOS}(x,\, y,\, \mathrm{eV}) d(\mathrm{eV})$ scalar fields. The latter one does not have spatially confined areas with high values. Surface of constant value for $\mathrm{STM}(x, y, \mathrm{eV})$ represent itself as smooth surface continuous at every point above model crystal slab.

The removal of single host atom leads to rearrangement of a few atoms in surface bi-layer of Ge(111)-(2×1) reconstruction, which is clear from Figs. 1a and 2. Thus the localization radii of single vacancy is not one unit cell anymore, and LDOS is noticeably disturbed inside this area (Fig. 1b). The spatial extent of perturbation

[1)]e-mail: SavinovSV@mail.ru

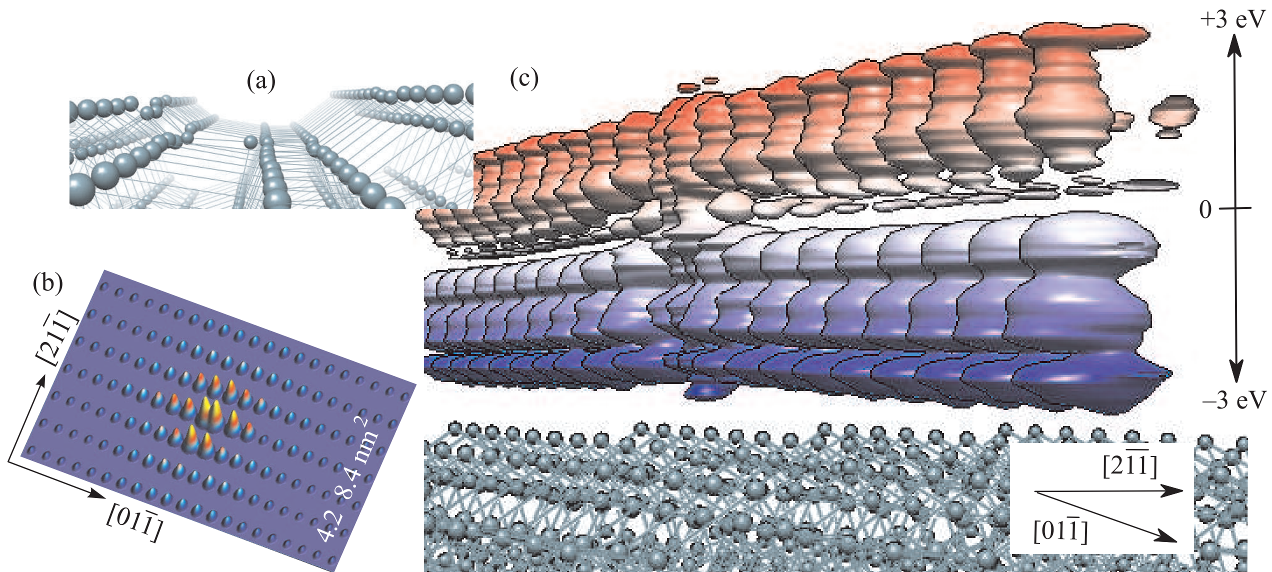

Fig. 1. Properties of Ge(111)-(2×1) surface in vicinity of surface vacancy. Relevant crystallographic directions are shown by marked arrows. (a) – Crystal lattice around vacancy. Arrow indicates the place from which Ge atom was removed. Atoms in a few rows have changed their positions. (b) – Quasi-3D distribution of surface LDOS. LDOS value is coded both by color and by height. LDOS disturbance spreads along π-bonded row ([01$\bar{1}$] direction) for at least 40 Å. All seven π-bonded rows, used in calculations, are disturbed. (c) – Surface LDOS(x, y, eV) field is shown by surface of constant value colored by applied bias voltage. LDOS is disturbed by the presence of vacancy quite far from the defect

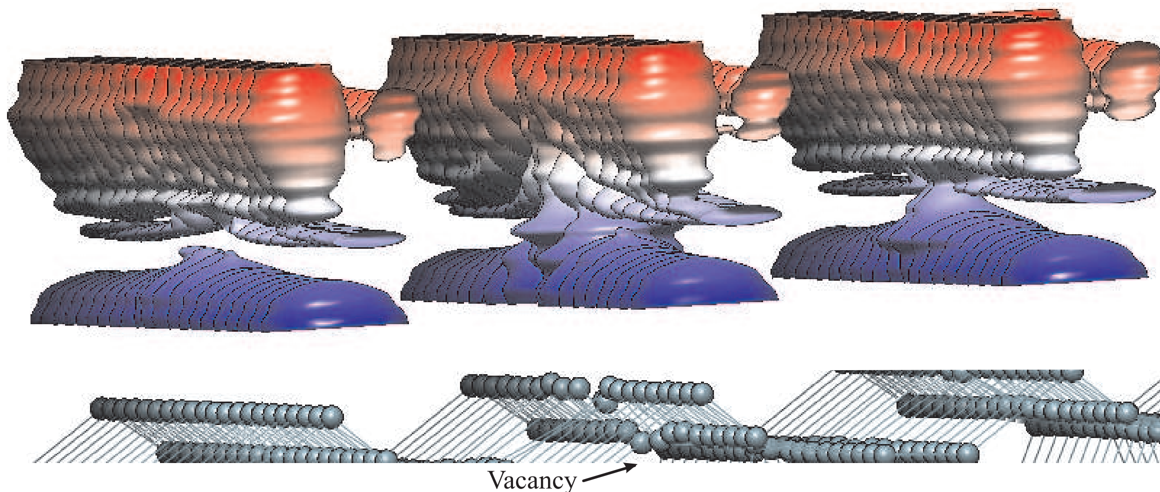

Fig. 2. Surface LDOS(x, y, eV) above Ge(111)-(2x1) surface in vicinity of surface vacancy. Arrow indicates the place from which Ge atom was removed. Atoms in a few rows have changed their positions. LDOS(x, y, eV) field is shown by surface of constant value colored by applied bias voltage. Band gap closure in two π-bonded rows adjacent to vacancy is apparent

along π-bonded rows ([01$\bar{1}$] direction) is about 40 Å, while in direction perpendicular to π-bonded rows ([2$\bar{1}\bar{1}$] direction) all seven atomic rows (also $\sim$ 40 Å) used in calculations are influenced by the defect – Fig. 1b.

It is known that LDOS of Ge(111)-(2×1) surface in band gap region is governed by non-occupied π^* surface states band [3]. As we have already shown the presence of donor impurity atom in surface bi-layer locally destroys the conditions for surface states formation and, besides this, leads to closure of band gap in vicinity of the defect [2]. Very similar situation can be observed in case of single vacancy – Figs. 1c and 2. The band gap is fully closed in two π-bonded rows, neighboring to vacancy.

In contrary to donor atom case there is no apparent split state in the band gap in vicinity of surface vacancy. Although STM image also has quasi-1D character its dependence on applied bias is much more complicated.

DFT methodology gives one a nice opportunity to analyze the local structure of Khon–Sham wave-

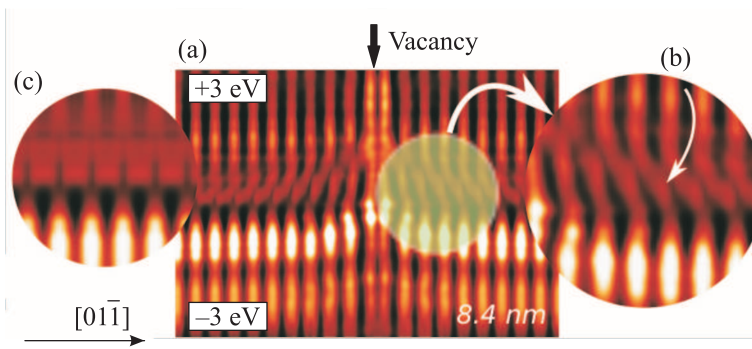

Fig. 3. (a) – Cross-section of surface LDOS(x, y, eV) along (x, eV) plane, containing vacancy. The position of vacancy along π-bonded row is indicated by black arrow. (b) – Zoomed in area of (a). (c) – The same as (b) for clean Ge(111)-(2×1) surface

functions. In Fig. 3 we present the cross-section of LDOS(x, y, eV) field along (x, eV) plane, which contains vacancy. Vertical bright stripes correspond to increased LDOS above dimers of π-bonded rows of Ge(111)-(2×1) reconstruction. Dark "horizontal" stripe in the middle reflects the presence of fundamental band gap (Fig. 3). It can be seen that band gap is disappearing as one comes closer to vacancy along π-bonded row.

Another interesting fact concerns atomic orbitals hybridization. In vicinity of vacancy it differs drastically from that far away from the defect. To illustrate this observation part of Fig. 3a is zoomed in to Fig. 3b. Atomic orbitals in the band-gap energy range are visually going (when bias voltage is changing from −3 V to +3 V) to the next row (Fig. 3b, thin white arrow), not to the nearest one. This is completely different from clean Ge(111)-(2×1) surface. The latter case is illustrated in Fig. 3c and atomic row is apparently going (from bottom to top) to the nearest row.

We would like to note, that namely this way of data representation for spectroscopic STM result is probably the most suitable for the task of individual defect identification. It could be more informative then the typical "LDOS at the point" method, and at least, both methods can be used together. One can see there is some kind of "band bending" in vicinity of atomic defect (Fig. 2a), which is characteristic of defect kind and its position in atomic lattice.

The main underlaying idea of DFT method is to build directly from atomic orbitals the spatial distribution of LDOS. As LDOS is calculated one can model STM/STS measurements, in particular it is possible to analyze the dependence LDOS(eV) at specific points above model slab. Thus we can compare LDOS(eV) averaged within small area (exactly the same way as experimental STM data is treated) above different atomic size defects.

The results of such comparison are depicted in reach of features Fig. 4. LDOS(eV) curves are shown for three

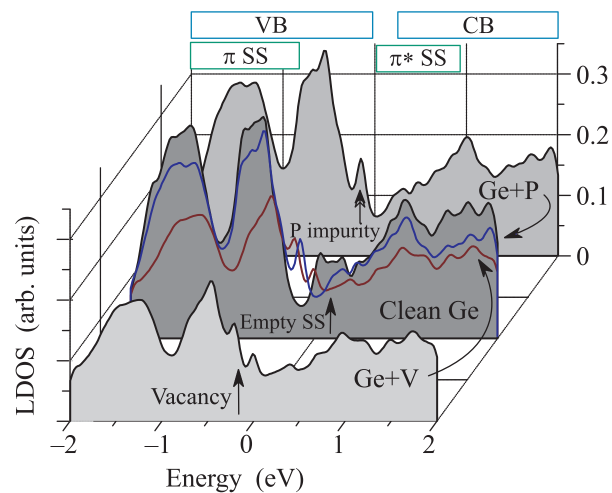

Fig. 4. Calculated dependence LDOS(eV) in three different cases: above clean Ge(111)-(2×1) surface; above individual vacancy (Ge+V); above P donor impurity (Ge+P). Surface band structure is schematically shown at the top of image, where SS stands for surface states, VB and CB stands for valence and conduction band respectively. The contribution from empty SS band to LDOS above clean surface is marked by white arrow. Split state at VB top originating from P donor impurity as well as states "created" by vacancy are marked by black arrows. All three curves are superimposed on the slice, corresponding to clean Ge case to allow easy estimation of LDOS Differences

cases: phosphorus (P) donor impurity atom, single vacancy (V) and clean defect-less surface. What is important is that in all three calculations we have used exactly the same set of parameters for Ge host atoms: basis orbitals, pseudo-potentials and crystal cell etc. Thus, the difference in LDOS is reflecting the influence of different defects.

In Fig. 4 three LDOS(eV) (dI/dV(V) from experimentator's point of view) dependencies, averaged within four unit cells of Ge(111)-(2x1) reconstruction, are depicted as grayed planes which are shifted for the sake of clarity. Curves for "Ge-donor" and "Ge-vacancy" cases are also superimposed on "clean Ge" curve. Surface band structure is schematically shown at the top of figure. The relative positions of valence (VB), conduction (CB) and occupied π and non-occupied π^* surface states bands are plotted as shaded rectangles. Within approximations of our model the bottom of π^* surface states band is located at the very top of valence band [2] and this is in full agreement with photoemission study [3]. The fundamental band gap is fully covered with non-occupied π^* SS band. It results in characteristic plateau above Fermi level on "clean Ge" curve. This plateau is absent both in case "Ge-donor" and "Ge-vacancy". At the same time additional peaks are resolved in LDOS(eV) right below Fermi level: single peak for "Ge-donor" and two peaks for "Ge-vacancy" (see superimposed curves in Fig. 4).

The main conclusion that can be readily drawn based on comparison of curves in Fig. 4 is that simple crystal structural defect, such as individual vacancy, affects surface electronic structure to the extent comparable with the influence of doping atom. Indeed, besides altered band structure in band gap region, LDOS inside the *whole* valence (VB) and conduction bands (CB) is lower above vacancy then both above the clean surface and above donor impurity (see superimposed curves in Fig. 4).

We have already reported both experimental observation [4] and theoretical first principles [2] confirmation of LDOS spatial oscillations (SO) existence around individual impurity atom on Ge(111)-(2×1) surface. Strong hybridization of atomic orbitals leads to LDOS SO formation. The same stands for surface vacancy. In Fig. 5 we show quasi-3D presentation of LDOS(x, y) spatial distribution at tunneling bias equal to 0.2 eV. The value of LDOS is coded both by color (the higher value – the brighter image) and by height. In contrast to the case of donor impurity atom, where atomic lattice disturbance was relatively low, in present case of surface vacancy, the electronic structure is perturbed in a few π-bonded atomic rows. We suppose this fact is mostly caused by geometrical lattice distortions. Spatial frequency of LDOS SO increases with increase of positive tunneling bias. LDOS SO disappear at bias higher then 0.6 V, similarly to the case of donor impurity. The LDOS SO

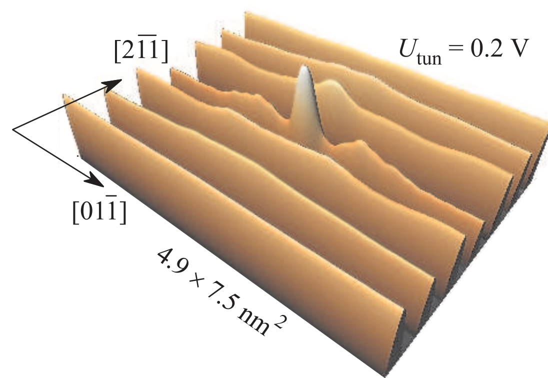

Fig. 5. Spatial oscillations of LDOS(x, y) in vicinity of individual atomic vacancy on Ge(111)-(2×1) surface. Tunneling bias voltage is 0.2 V. Relevant crystallographic directions are shown by marked arrows

can be observed in bias range, where π^* non-occupied surface states band resides.

We can not unambiguously deduce the dispersion law for LDOS SO, although some facts rules us to the conclusion about the quasi-linear character of dispersion law.

We are aware of the necessity of the detailed comparison of DFT results with experimental STS data, but this is the subject for another publication.

Conclusion. In conclusion, by numerical modeling we showed that the simplest surface defect strongly influences surface LDOS structure noticeably far ($\sim$ 40 Å) from the defect. We also demonstrate the strong difference of surface LDOS structure above surface defects of different kind. We have proved theoretically by first principles calculations that spatial oscillations of LDOS exist around individual surface vacancy in the same tunneling bias range as in case of donor doping atom on Ge(111)-(2×1) surface. The LDOS SO can be observed in bias range, where π^* non-occupied surface states band resides.

This work has been supported in part by the grants of Russian Foundation of Basic Researches and computing facilities of M.V. Lomonosov Moscow State University Research Computing Center.

1. E. Artacho, D. Sanchez-Portal, P. Ordejon et al., Phys. Stat. Sol. B **215**, 809 (1999).
2. S. V. Savinov, S. I. Oreshkin, and N. S. Maslova, Pis'ma v ZhETF, **93**(9), 579 (2011).
3. J. M. Nicholls, P. Maartensson, and G. V. Hansson, Phys. Rev. Lett. **54**, 2363 (1985).
4. D. A. Muzychenko, S. V. Savinov, V. N. Mantsevich et al., Phys. Rev. B **81**, 035313 (2010).