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Electronic structure of Ge(111)-(2×1) surface in the presence of doping atoms. Ab initio analysis of STM data

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We present the result of first principles modeling of the Ge(111)-(2×1) surface electronic structure in the presence of donor doping atom at certain position in the surface bi-layer of (2×1) reconstruction. We briefly compare these results with the data of experimental low temperature STM investigations. *Ab initio* calculations demonstrate that doping atom strongly disturbs local electronic structure. The separate state, most probably split off conduction band, appears in the bandgap. Surface LDOS reveals spatial oscillations in vicinity of foreign atom. We also show that the spatial extent of non-negligible inter-atomic interaction between neighboring donor atoms is not less then 70 Å.

Electronic properties on elemental semiconductors (in particular Ge) have attracted substantial interest since they were historically the first semiconductors applicable in the technology. The cleavage along (111) natural cleavage plane allows one to obtain surface with well known (2×1) type of reconstruction [1]. This surface can serve as the test bench for both experimental STM/STS studies of individual atomic defects, and theoretical modeling.

In 1980s, both photoemission studies [2] of doped Ge single crystals and theoretical calculations [3] have revealed the existence of separate π occupied and π^* non occupied p_z derived bands for the Ge(111) surface electrons. For heavily doped Ge a partial occupation of π^* band was observed. Due to surface band bending occupied surface states can exist *above* the bottom of π^* band [2]. The value of Ge(111) surface band gap has been explored by means of STM and STS [4] and discussed by theorist [5]. At the same time until now there have been only one report [6] on the experimental observations of effects directly related to the existence of unoccupied surface states π^* band on the Ge(111)-(2×1) surface. We have reported on our investigation of the non-occupied surface states on *in situ* cleaved Ge(111)-(2×1) surfaces by means of low-temperature STM/STS under UHV conditions. The presence of the non-occupied surface states is observed to induce local density of electronic states (LDOS) spatial oscillations in the vicinity of domain boundary or individual impurity atom on Ge(111)-(2×1) surface in the energy range of unoccupied surface states π^* existence [6]. Experimental observation of quasi-1D surface screening around atomic defects on Ge(111)-(2×1) surface, as well as the analysis of tunneling bias dependent behavior of impurity' STM image were discussed by us in [7].

To clarify the physical nature of experimentally (STM/STS) observed effects we have performed first principles calculations by means of DFT method in the LDA approximation as implemented in SIESTA package [8]. Details will be published elsewhere. The use of strictly localized numeric atomic orbitals allows us to perform modeling of large surface cell, which amounts up to 4×35 cells of elementary 2×1 reconstruction (2520 atoms). The model structure consists of Ge(111)-(2×1) surface slab. All dangling Ge bonds at the bottom surface are terminated with H atoms, and one Ge atom is substituted by the phosphorus (P) atom. The geometry of the structure was fully relaxed, until atomic forces have became less then 0.01 eV/Å. Afterwards the surface band structure and spatial distribution of local density LDOS were calculated.

1. Surface geometry and band structure. The results of DFT modeling can be summarized as follows.

The Ge(111) surface reconstruction of (2×1) type causes the presence of occupied π and unoccupied π^* bands of surface states in the bandgap of projected bulk band structure (Fig. 1). Surface states are highly dispersive along $\overline{\Gamma} - \overline{\mathrm{J}}$ line of 2D surface Brillouin zone. Bands are flat along $\overline{\mathrm{J}} - \overline{\mathrm{K}}$ line(Fig. 1). Worth noting that the bottom of π^* surface band is located in very close proximity to Fermi level [2, 7], which in its own turn is aligned with the top of bulk valence band in case of Ge(111) surface [9]. Fine details of band structure around Fermi level on Ge(111)-(2×1) surface are still remaining unclear. DFT modeling can not *in principle* give the correct values for band gaps, nonetheless the

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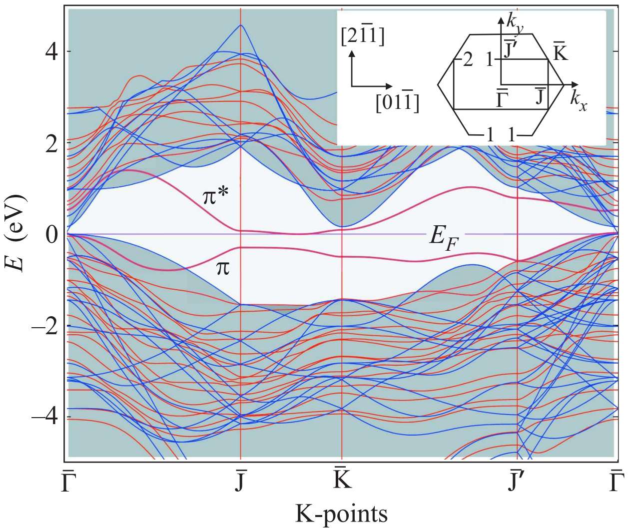

Fig. 1. Surface band structure of clean Ge(111)-(2×1) surface. Shaded area corresponds to projected bulk band structure. Occupied π and unoccupied π^* surface states bands are clearly visible in projected band gap. Inset shows the relevant details of Ge(111)-(2×1) surface model

alignment for different energy levels can be correct. Let us stress the fact that in DFT framework we are also incapable to take into account the effects of surface band bending [2, 7, 10]. The calculated surface band structure should be treated in the DFT framework as the correct one for any kind of bulk doping (n- or p-type and any doping ratio). It is in general possible to introduce into the calculations the electric field, which models the effects of band bending. At the same time we could not find any substantial difference in the results of calculations with and without compensating electric field.

We have proven that the atom of substitutional donor impurity P *does not* occupy the same place in the lattice as the Ge atom it substitutes, though the displacement is not very large (Fig. 2a). This is not an unexpected behavior, but, surprisingly, we could not find in the literature any statement explicitly confirming this fact.

The model of Ge(111)-(2×1) surface reconstruction [1] with π-bonded chain rows can be readily proven by the analysis of spatial distribution of the system's charge. The π bonds along chain rows are imaged as bridges above upper rows of (2×1) reconstruction in the spatial distribution of negative values of differential charge (Fig. 2b). Ge-Ge covalent bonds for atoms outside upper π-bonded rows are seen as ellipsoidally shaped volumes of increased electron density (i.e. negative charge) located approximately in the middle in between neighboring Ge atoms. π bonds are broken in immediate vicinity of doping atom, and the charge distribution in this area is quite complicated.

2. Surface density of states. The most interesting result of our DFT modeling is the determination of spatial distribution of local density LDOS above the surface. Namely this quantity is relevant for STM observations' interpretation. In the DFT framework surface LDOS can be expressed as

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

where Ψ are Khon-Sham eigenfunctions, $\tilde{\delta}$ is smearing function, E_i are Khon-Sham eigenvalues, and summing is evaluated at the plane located a few angstroms above the surface. This way we can calculate and plot surface LDOS $\rho(x, y,\mathrm{eV})$ distribution (Fig. 3). Smearing here should be considered as the very essential part of procedure. To the best of our knowledge this is the first time when this type of data representation is used.

LDOS is depicted above single upper π-bonded row (the nearest to impurity atom) to make the image readable. Scalar field of LDOS $\rho(x, y,\mathrm{eV})$ is represented as a surface of constant value. In our particular case higher/lower values of LDOS are located inside/outside the volume bounded by this surface.

The LDOS spatial distribution reveals quasi-1D character. Areas with high LDOS values are *completely localized above* upped π-bonded rows of (2×1) reconstruction, while low LDOS value areas are located in between π-bonded rows. This leads to STM imaging of only any other (namely upper) surface π-bonded row [4]. At the same time LDOS is disturbed by foreign atom in a few neighboring π-bonded rows. This is why we can not treat Ge(111)-(2×1) surface as being purely one dimensional system. Speaking in tight-binding language, although hopping $t_{\|}$ along π-bonded rows should be approximately an order of magnitude larger, than in hopping orthogonal direction $t_{\perp}$, the latter one in not negligible. Relatively high value of about 0.25 was obtained for $t_{\perp}/t_{\|}$ ratio by the best fit procedure in [6].

STM image of (sub-)surface impurity on Ge(111)-(2×1) surface to the zeroth approximation looks like quasi-1D protrusion at negative tunneling bias and as a depression at positive bias [7]. As it can be seen from Fig. 3 there is a state in the bandgap, which is most probably split off the conduction band. It is located just below the Fermi level (Fermi level is located at the very top of split state). At negative bias it gives rise to excessive tunneling current above upper π-bonded row of (2×1) reconstruction in vicinity of doping atom. Its influence vanishes when bias goes deeper into filled bulk valence band or when STM tip moves away from P impurity atom. The existence of aforementioned split state gives an explanation to the experimentally observed shape and bias dependent behavior of P donor impurity on

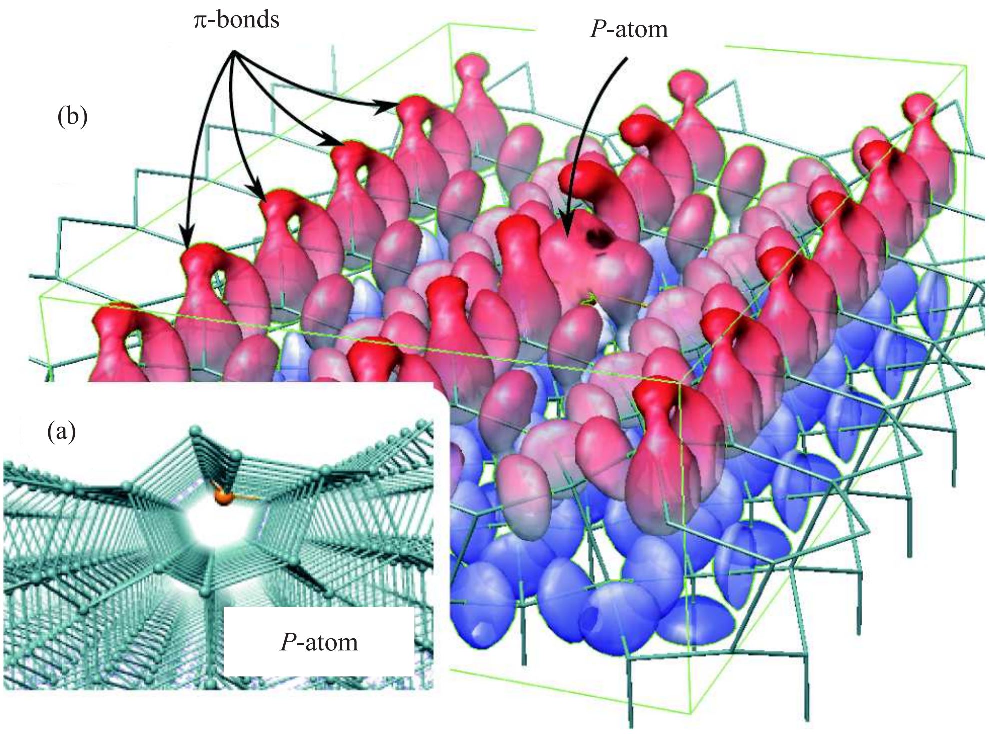

Fig. 2. (a) The geometry of relaxed Ge(111)-(2×1) surface. P impurity atom is shown by big sphere. (b) Spatial distribution of negative differential charge on Ge(111)-(2×1) surface around P impurity atom. Color scale corresponds to the distance measured from the upper plane of charge distribution, i.e. plane at which non-zero values of charge are still observed

freshly cleaved Ge(111)-(2×1) surface in the negative bias range.

More detailed analysis reveals that split state originates from P donor impurity atom localized state.

Atomic orbitals of Ge atoms next to impurity atom are strongly hybridized in the positive bias voltage range, where π^* surface states band are located. In Fig. 3 this gives an impression of some upward "band bending". This results in decreasing of LDOS above upper π-bonded row in this range of positive bias. Noticeable exception occurs right above impurity atom where LDOS is still high (see Fig. 3). As a consequence P dopant atom looks on STM images as bright spot superimposed on quasi-1D depression in certain range of positive tunneling bias.

In the DFT framework the contributions from different atomic orbitals/atoms to Khon-Sham (KS) wave function (WF) can easily be separated. This is "by design". The procedure does not have deep physical meaning (nor Khon-Sham WF have), but allows to visualize, for example, the localization of impurity atom's WF. The illustration is given in Fig. 3, where contribution from atomic WF of P impurity atom is specifically shown by different color. Impurity WF are localized within two or three unit cells from impurity atom itself.

We would like to note that we can also readily analyze spatial localization of full KS WF, and for some range of positive bias (π^* surface states band range) KS WF are indeed localized near the surface.

Strong hybridization of atomic orbitals has one lot more important consequence. It leads to the appearance of spatial oscillations (SO) of surface (i.e. as measured by STM) LDOS in vicinity of impurity atom (Fig. 4). LDOS SO can be observed in a few neighboring atomic rows in vicinity of impurity atom. The existence of LDOS SO is not obvious from Fig. 3. Ge atoms AO are strongly hybridized, and the spatial picture of hybridization apparently depends on bias voltage. LDOS 3D field is obtained in numerical modeling, noise level is low (as is often opposite for experimental STM/STS data). We can easily filter out atomic corrugation spatial frequencies and stress relatively weak low frequency features. The result is depicted in Fig. 4. It shows the spatial distribution of numerical LDOS (which corresponds to tunneling conductivity dI/dV(eV) STM signal) at certain value of positive bias. Now LDOS SO are obvious. The image is quasi-3D presentation of LDOS values at certain plane above the surface. The LDOS values are coded by surface height. This to the most extent corresponds to the $dI/dV(x, y,\text{eV})$ tunneling conductivity STM images (or modulation STM images) [6].

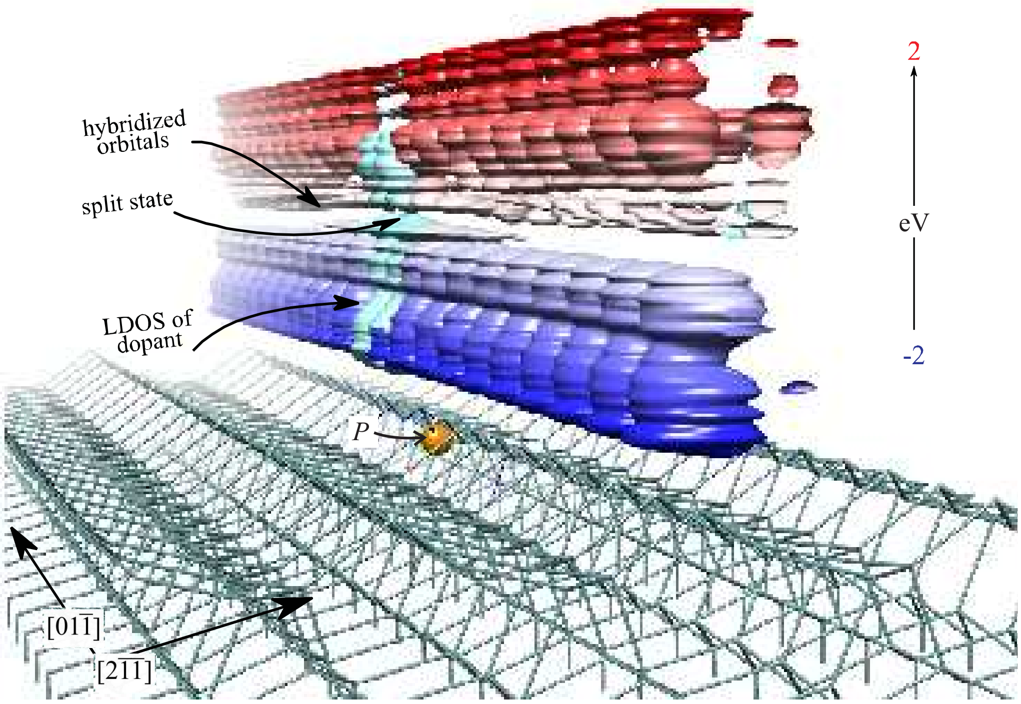

Fig. 3. Spatial distribution of surface LDOS. 3D field $\rho(x, y, \mathrm{eV})$ is shown as constant value surface. Areas of interest, such as strongly hybridized Ge atomic orbitals, split state in the band gap and area of P donor impurity wave functions localization are marked by arrows. Fermi level is located at the very top of split state. It is not explicitly shown because it will render the image hardly readable. Relevant crystal directions are also shown

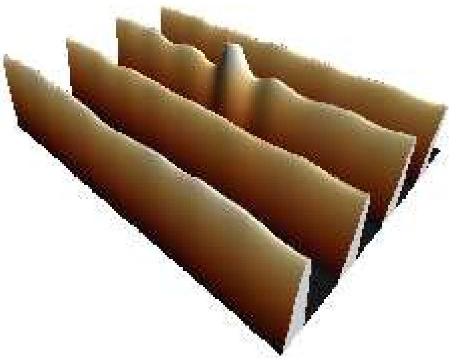

Fig. 4. Quasi-3D representation of surface LDOS. Spatial oscillations in vicinity of P donor impurity atom are clearly visible. A few atomic rows are disturbed

The period of LDOS SO decreases as tunneling bias increases. When tunneling bias is leaving the range, where π^* unoccupied states exists, LDOS SO disappear. At the bottom of π^* band LDOS SO period is becoming very large (infinite in the limit). At the top of π^* band (or slightly lower) LDOS SO are suppressed by the tunneling into the bulk unoccupied states. The dispersion law for LDOS SO along π-bonded rows is almost linear-like. Wwe must emphasize the fact, that the overall impression (not the shape), which makes dispersion curve, strongly depends on a way of its calculation. We would like to leave the detailed discussion for the future publications.

In present work we deal with the oscillation of local density of electronic states, not with Friedel oscillations. There is long standing inaccuracy in terminology which sometimes even leads to misinterpretation of results. Accurately speaking, Friedel oscillations are the oscillation of *charge* density around foreign atom: "the density of screening charge about the point impurity" [11]. In other words Friedel oscillations are the effect arising from screening of localized charge. This interpretation implies that Friedel oscillation can be observed by STM method only for electronic states *below* Fermi level, or in filled states image. This, indeed, is a case. We have reported low temperature STM observation of Friedel oscillations in vicinity of Te impurity atom of GaAs(110) surface. We have also discussed the conditions under which this observation is possible [12].

Now, by means of DFT modeling, we show that the presence of foreign atom in the surface layer of Ge(111)-(2×1) reconstruction results in the appearance of spatial oscillations of local density of electronic states. In our particular case these oscillations can be observed both experimentally [6] and theoretically (see. Fig. 4) *above* Fermi level, or in empty states STM image. The frequency of LDOS SO is increasing with positive tunneling (energy) increase.

The LDOS oscillation are more general case then Friedel oscillations. For example, LDOS oscillations below Fermi level will lead to Friedel oscillations. We suppose that more extended discussion is beyond the scope of present work.

Our calculations allow to estimate the bias dependent shift of atomic rows on Ge(111) surface with (2×1) type of reconstruction. DFT method predicts the shift of π-bonded rows in $[2\overline{1}\overline{1}]$ direction by approximately 0.9 Å with changes of bias voltage from filled to empty states. This value is noticably less than the value of 1.9 Å determined from experimental STM data analysis [13], but in accordance with reports in the literature [5]. The situation is even worse for the shift of atomic dimers inside π-bonded row along $[01\overline{1}]$ direction. The experimental value amounts almost full period 3.8 Å, while DFT prediction value is not more then 1 Å. Most probably this difference reflect the difference between the model and real tunneling processes. In reality we always have to take into account different effects which complicates the description. For example, charge accumulation, tunneling with phonon excitation etc.

Electronic properties of semiconductors can be tuned by changing their chemical dopig level. Typical doping level is in the range of $10^{15-18}\,\mathrm{cm}^{-3}$ bulk concentration. Assuming uniform doping atoms spatial distribution, this leads to $10^{10-12}\,\mathrm{cm}^{-2}$ surface impurity concentration. It is order of magnitude less then the concentration deduced from our model surface slab size. So we did the check of our results against the effects of inter doping atoms interaction. The conclusion is the following. To reliably predict electronic structure along π-bonded rows of Ge(111)-(2×1) surface one needs at least 70 Å separation between neighboring impurity atoms in $[01\overline{1}]$ direction. If this distance is too short, one will get strong interaction. Due to periodic boundary conditions applied in DFT method, the band structure will be hopelessly disturbed. Let us say, for model slab with dimensions of 4×7 cells of 2×1 reconstruction (28 Å×28 Å) there will be a hole ($\rho(x, y, \mathrm{eV}) = 0$) in LDOS of unoccupied states in vicinity of impurity atom, which is rather non-physical. The derived value of interaction distance 70Å is in nice correspondence with the value of Bohr radius for shallow impurity.

Due to purely technical limitations (luck of sufficient computational resources) we can not accurately determine interaction distance in $[2\overline{1}\overline{1}]$ direction, orthogonal to the direction of π-bonded rows. Based on the estimation that hopping element in this direction $t_\perp$ is approximately 10 times smaller than $t_\parallel$, we can guess that 4–5 atomic rows can be the lower bound for estimation.

We did not put many numbers in the text intentionally. Though we can claim even semi-quantitative agreement between our experimental data and DFT calculations results we restrict ourselves to *qualitative only* discussion.

In summary, we have found that the presence of donor impurity atom in surface bi-layer of Ge(111)-(2×1) surface leads to the appearance of split state in the band gap and to strong hybridization of atomic orbitals for Ge atoms located in vicinity of impurity. This hybridization in its turn causes the appearance of LDOS spatial oscillations (not Friedel oscillation). We have estimated the distance at which the interaction between impurity atoms strongly modifies the band structure.

Our finding makes very important link between first principle description of solid state body and diagram technique based theoretical methods. The latter naturally predicts both the existence LDOS SO around atomic defects and the appearance of split states. We have prove that the former can do this too, providing at the same information on spatial LDOS distribution with "atomic" resolution.

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