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Many-particle interaction in tunneling spectroscopy of Ge adatoms on Ge(111) surface

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We report on the direct observation by means of low temperature scanning tunneling microscopy and spectroscopy (STM/STS) of additional peculiarities in the local tunneling conductivity caused by the presence of low-dimensional structures – Ge ad-atoms and domain wall on the Ge(111) surface. We also proposed theoretical model to explain the physical reason of observed peculiarities formation. We consider such systems to be a good candidates for charge and spin configurations formation by means of STM/STS technique.

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1. Introduction. Electronic properties of the elemental semiconductors Si and Ge surfaces attract a lot of interest due to their technological relevance as well as due to their fundamental scientific importance. Ge (111) surface has been intensively investigated because it corresponds to the natural cleavage plane. Cleaved Ge (111) surface demonstrates typical 2×1 reconstruction and consists of Ge atoms π-bonded chains along the $[01\bar{1}]$ direction [1]. Scanning tunneling microscopy/spectroscopy (STM/STS) technique are ideal tools for investigation of electronic structure of reconstructed Ge surface [2, 3]. STM images of the Ge (111) 2×1 surface consists of various domains that have different atomic arrangement [4]. The influence of domain walls, single and coupled impurity atoms on the local density of surface electronic states modification was analyzed by means of STM/STS technique [5]. Until now however, there have been no direct observations of effects related to the local density of surface electronic states modification due to the single and interacting Ge ad-atoms.

Theoretical self-consistent approach based on Keldysh diagram technique [6] have been applied to analyze non-equilibrium effects and tunneling current spectra for single deep and shallow impurities [7] and for the system of two weekly coupled impurities [8] in the presence of Coulomb interaction. Theoretical approach based on the Heisenberg equations for localized states electron filling numbers taking into account local electron density correlations in all orders was successfully applied for electronic transport analysis in the multi-level impurity atoms and strongly coupled impurities [9–11].

Here we report on detailed investigations of the single and coupled ad-atoms on the *in situ* cleaved Ge (111) surface by means of low-temperature ultra-high vacuum STM/STS. We revealed additional peculiarities in the local tunneling conductivity caused by the presence of Ge ad-atoms. We also proposed theoretical model based on the pseudo-particle operators with constraint on the physical states which gave us possibility to explain the physical reason of observed peculiarities formation.

2. Experimental. *In situ* crystal cleavage and STM/STS measurements were performed by means of low-temperature ultra high vacuum setup ($T_{\mathrm{sample}} = 4.2\,\mathrm{K}$). The ultra high vacuum system is decoupled from the building by a specially designed vibration isolation floor for optimal measurement conditions. In all the experiments tungsten tips electrochemically etched were used. STM topographic images were obtained in the constant current mode. The local $I(V)$ curves above the flat surface, domain wall, single and coupled adatoms were recorded with open feedback loop. In all the text and in the figure captions tunneling voltages are always given with respect to the sample.

$1.5\times1.5\times5\,\mathrm{mm}^3$ Ge bars with their long axis aligned with the (111) direction were cleaved *in situ* at room temperature in the sample preparation chamber at a pressure around $5 \cdot 10^{-11}$ mbar. The Ge samples under investigation were doped with Ga atoms at a doping level of $2 \cdot 10^{16}\,\mathrm{cm}^{-3}$, resulting in p-type bulk conductivity. The freshly cleaved samples were transferred to the STM measurement chamber. During the crystal

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cleavage procedure a limited number of ad-atoms were formed on the Ge surface. Single and coupled Ge ad-atoms were analyzed by means of STM/STS technique. Fig. 1 demonstrates a typical topographic constant current STM image of a single ad-atom, two interacting ad-atoms and domain wall on the clean Ge (111) 2×1 surface. The topographic image demonstrates that the freshly cleaved Ge surface is atomically flat.

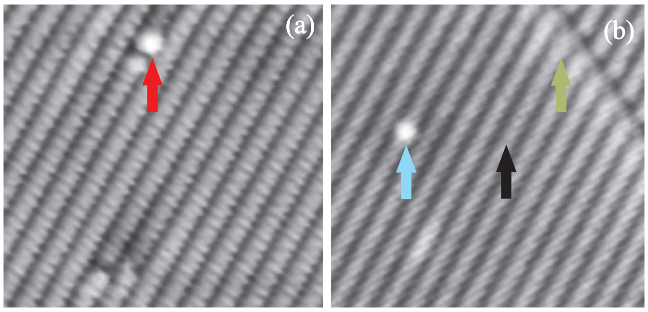

Fig. 1. (Color online) Constant current Ge (111) 2×1 surface STM image (tunneling current $I = 20\,\mathrm{pA}$, $eV = +0.5$ (a), $eV = +0.8\,\mathrm{V}$ (b)). Red arrow demonstrates interacting ad-atoms, blue arrow – single ad-atom, green arrow – domain wall and black arrow corresponds to the STS measurements above the clean surface

We performed STS measurements of local tunneling conductivity above the single ad-atom, two interacting ad-atoms, domain wall and clean Ge (111) 2×1 surface. Obtained results of tunneling current conductivity measurements are shown in the Fig. 2.

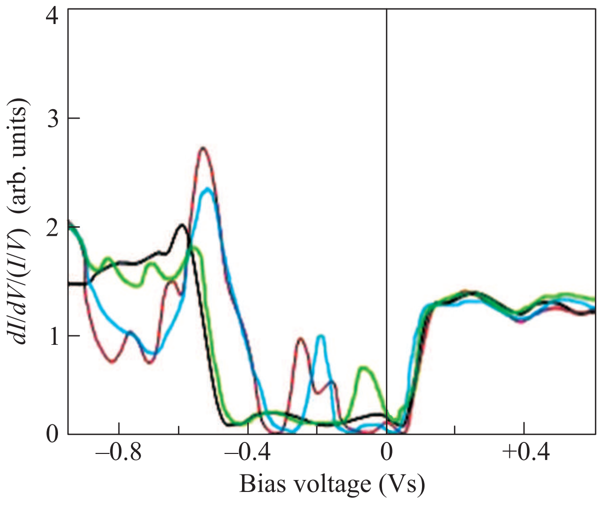

Fig. 2. (Color online) $dI/dV(V)$ spectra at the four correspondingly labeled locations on the Ge (111) 2×1 surface in Fig. 1

To analyze experimentally observed results we present in the following Section theoretical model that accounts for the main properties of the experimentally observed local tunneling current spectra peculiarities. Proposed theoretical model is based on the pseudo-particle operators with constraint on the physical states [12].

3. Theoretical model. In the case of single ad-atom on the Ge surface we consider a model system of localized state with the single particle energy level ε connected to the two leads (subsurface and STM tip). The Hamiltonian in this case can be written as:

$$\hat{H} = \hat{H}_0^1 + \hat{H}_{\mathrm{tun}}^1,$$
$$\hat{H}_0^1 = c_\sigma^+ c_\sigma \varepsilon + U n_\sigma n_{-\sigma} + \sum_{\sigma,k} c_{k\sigma}^+ c_{k\sigma}\varepsilon_k + \sum_{\sigma,p} c_{p\sigma}^+ c_{p\sigma}\varepsilon_p,$$
$$\hat{H}_{tun}^1 = \sum_{\sigma,k} t_k (c_{k\sigma}^+ c_\sigma + c_\sigma^+ c_{k\sigma}) + \sum_{\sigma,p} t_p (c_{p\sigma}^+ c_\sigma + c_\sigma^+ c_{p\sigma}), \quad (1)$$

where operator c_σ creates an electron in the ad-atom with spin σ, ε is the energy of the single electron level in the ad-atom, $t_{k(p)}$ is the tunneling coupling between the ad-atom and tunneling contact leads, $n_\sigma = c_\sigma^+ c_\sigma$, and U is the on-site Coulomb repulsion of localized electrons. In such a system two electrons can be localized at the same time and four different electronic configurations are possible $|00\rangle$, $|0\uparrow\rangle$, $|0\downarrow\rangle$, and $|\uparrow\downarrow\rangle$ with corresponding energies 0, ε, ε, and $2\varepsilon + U$.

In the case of two interacting ad-atoms on the Ge surface we consider a model system of two coupled localized states with the single particle levels ε_1 and ε_2 connected to the tunneling contact leads. The Hamiltonian can be written as:

$$\hat{H} = \hat{H}_0^2 + \hat{H}_{\mathrm{tun}}^2,$$
$$\hat{H}_0^2 = \sum_\sigma c_{1\sigma}^+ c_{1\sigma}\varepsilon_1 + \sum_\sigma c_{2\sigma}^+ c_{2\sigma}\varepsilon_2 + U_1 \widehat{n}_{1\sigma}\widehat{n}_{1-\sigma} + {} + U_2 \widehat{n}_{2\sigma}\widehat{n}_{2-\sigma} + \sum_\sigma T(c_{1\sigma}^+ c_{2\sigma} + c_{2\sigma}^+ c_{1\sigma}),$$
$$\hat{H}_{\mathrm{tun}}^2 = \sum_{\sigma,k} t_k (c_{k\sigma}^+ c_{1\sigma} + c_{1\sigma}^+ c_{k\sigma}) + {} + \sum_{\sigma,p} t_p (c_{p\sigma}^+ c_{2\sigma} + c_{2\sigma}^+ c_{p\sigma}), \quad (2)$$

where operator $c_{l\sigma}$ creates an electron in the ad-atom i with spin σ, ε_l is the energy of the single electron level in the ad-atom i, T is the inter-ad-atoms tunneling coupling, $n_{l\sigma} = c_{l\sigma}^+ c_{l\sigma}$, and $U_{1(2)}$ is the on-site Coulomb repulsion of localized electrons. When the coupling between ad-atoms exceeds the value of interaction with the leads, one has to use the basis of exact eigenfunctions and eigenvalues of coupled ad-atoms without the interaction with the leads. In this case all energies of single- and multi-electron states are well known.

• One electron in the system: two single electron states with the wave function

$$\psi_i^\sigma = \mu_i|0\uparrow\rangle|00\rangle + \nu_i|00\rangle|0\uparrow\rangle. \quad (3)$$

Single electron energies and coefficients μ_i and ν_i can be found as an eigenvalues and eigenvectors of matrix:

$$\begin{pmatrix} \varepsilon_1 & -T \\ -T & \varepsilon_2 \end{pmatrix}. \quad (4)$$

• Two electrons in the system: two states with the same spin $\sigma\sigma$ and $-\sigma-\sigma$ and four two-electron states with the opposite spins $\sigma-\sigma$ with the wave function:

$$\psi_j^{\sigma-\sigma} = \alpha_j|\uparrow\downarrow\rangle|00\rangle + \beta_k|\downarrow 0\rangle|0\uparrow\rangle + \\ + \gamma_j|0\uparrow\rangle|\downarrow 0\rangle + \delta_j|00\rangle|\uparrow\downarrow\rangle. \quad (5)$$

Two electron energies and coefficients α_j, β_j, γ_j, and δ_j are the eigenvalues and eigenvectors of matrix:

$$\begin{pmatrix} 2\varepsilon_1+U_1 & -T & -T & 0 \\ -T & \varepsilon_1+\varepsilon_2 & 0 & -T \\ -T & 0 & \varepsilon_1+\varepsilon_2 & 0 \\ 0 & -T & -T & 2\varepsilon_2+U_2 \end{pmatrix}. \quad (6)$$

• Three electrons in the system: two three-electron states with thewave function

$$\psi_m^{\sigma\sigma-\sigma} = p_m|\uparrow\downarrow\rangle|\uparrow\rangle + q_m|\uparrow\rangle|\uparrow\downarrow\rangle, \\ m=\pm 1. \quad (7)$$

Three electron energies and coefficients p_m and Q_m can be found as an eigenvalues and eigenvectors of matrix:

$$\begin{pmatrix} 2\varepsilon_1+\varepsilon_2+U_1 & -T \\ -T & 2\varepsilon_2+\varepsilon_1+U_2 \end{pmatrix}. \quad (8)$$

• Four electrons in the system: one four-electron state with energy $E_{\mathrm{IV}l} = 2\varepsilon_1+2\varepsilon_2+U_1+U_2$ and wave function

$$\psi_l = |\uparrow\downarrow\rangle|\uparrow\downarrow\rangle. \quad (9)$$

If coupled ad-atoms are connected with the leads of the tunneling contact the number of electrons in the dots changes due to the tunneling processes. Transitions between the states with different number of electrons in the two interacting ad-atoms can be analyzed in terms of pseudo-particle operators with constraint on the physical states (the number of pseudo-particles). Consequently, the electron operator $c_{\sigma l}^+$ $(l=1,2)$ can be written in terms of pseudo-particle operators as:

$$c_{\sigma l}^+ = \sum_i X_i^{\sigma l} f_{\sigma i}^+ b + \sum_{j,i} Y_{ji}^{\sigma-\sigma l} d_j^{+\sigma-\sigma} f_{i-\sigma} + \\ + \sum_{j,i} Y_i^{\sigma\sigma l} d^{+\sigma\sigma} f_{i\sigma} + \sum_{m,j} Z_{mj}^{\sigma\sigma-\sigma l} \psi_{m-\sigma}^+ d_j^{\sigma-\sigma} + \\ + \sum_m Z_m^{\sigma-\sigma-\sigma l} \psi_{m\sigma}^+ d^{-\sigma-\sigma} + \sum_m W_m^{\sigma-\sigma-\sigma l} \varphi^+ \psi_{m\sigma}, \quad (10)$$

where $f_\sigma^+(f_\sigma)$ and $\psi_\sigma^+(\psi_\sigma)$ are pseudo-fermion creation (annihilation) operators for the electronic states with one and three electrons correspondingly, $b^+(b)$, $d_\sigma^+(d_\sigma)$, and $\varphi^+(\varphi)$ are slave boson operators, which correspond to the states without any electrons, with two electrons or four electrons. Operators $\psi_{m-\sigma}^+$ describe system configuration with two spin up electrons σ and one spin down electron $-\sigma$ in the symmetric and asymmetric states.

Finally one can easily express matrix elements through the matrixes (4), (6), (8) eigenvectors elements [12]:

$$\begin{aligned} X_i^{\sigma 1} &= \mu_i,\ X_i^{\sigma 2} = \nu_i, \\ Y_{ji}^{\sigma-\sigma 1} &= \alpha_j\mu_i + \beta_j\nu_i, \\ Y_{ji}^{\sigma-\sigma 2} &= \delta_j\nu_i + \gamma_j\mu_i, \\ Y_{ji}^{\sigma\sigma 1} &= \nu_i,\ Y_{ji}^{\sigma\sigma 2} = \mu_i, \\ Z_{mj}^{\sigma\sigma-\sigma 1} &= p_m\gamma_j + q_m\delta_j, \\ Z_{mj}^{\sigma\sigma-\sigma 2} &= p_m\alpha_j + q_m\beta_j, \\ Z_{mj}^{\sigma-\sigma-\sigma 1} &= p_m,\ Z_{mj}^{\sigma-\sigma-\sigma 1} = q_m, \\ W_m^{\sigma-\sigma-\sigma 1} &= q_m,\ W_m^{\sigma-\sigma-\sigma 2} = p_m. \end{aligned} \quad (11)$$

The constraint on the space of the possible system states have to be taken into account:

$$\widehat{n}_b + \sum_{i\sigma} \widehat{n}_{fi\sigma} + \sum_{j\sigma\sigma'} \widehat{n}_{dj}^{\sigma\sigma'} + \sum_{m\sigma} \widehat{n}_{\psi m\sigma} + \widehat{n}_\varphi = 1. \quad (12)$$

Condition (12) means that the appearance of any two pseudo-particles in the system simultaneously is impossible. The further analysis of electronic transport properties through the single and coupled ad-atoms and $I(V)$ characteristics can be performed by means theoretical approach developed in [12]. We consider the energy levels of ad-atoms to be deep enough ($\varepsilon_i < 0$), so the following conditions are valid: $\varepsilon_i < 0$ and $\varepsilon_i + U < 0$. Moreover we'll consider the ad-atoms to have very close to each other energy levels. In the next Section we'll discuss the results of the proposed model application to the obtained experimental results.

4. Discussion. Let us now discuss the obtained results. Black line in the Fig. 2 corresponds to the measurements of local tunneling conductivity above the flat clean Ge (111) 2×1 surface. One can easily resolve the surface band gap without any additional peaks or oscillations caused by the presence of surface low-dimensional structures. Blue line corresponds to normalized tunneling conductivity measured above the single Ge ad-atom on the Ge (111) 2×1 surface. This curve reveals two additional peaks in the surface band gap in comparison with the tunneling current spectra measured above the flat surface. These peaks correspond to the transitions between the 2-electronic states and 1-electronic states and to the transitions between 1-electronic states and state without electrons. The peak which corresponds to the transitions between the 2-electronic states and 1-electronic states can be seen at the applied bias voltage equal to $\varepsilon + U$ and the peak which corresponds to the transitions between one-electronic states and state without electrons can be seen at the applied bias voltage equal to ε.

Red line demonstrates normalized tunneling conductivity measured above the two interacting Ge ad-atoms on the Ge (111) 2×1 surface. In this case one can find the splitting of the peak, which corresponds to the transitions between the 2-electronic states and 1-electronic states (the blue line $eV = \varepsilon + U$). Splitting and two peaks formation instead of one correspond to the transitions between 4-electronic state and 3-electronic states. For ad-atoms with different values of energy levels and Coulomb correlation values the energy of 4-electronic state can be written as $E_{\rm IV} = 2\varepsilon_1 + 2\varepsilon_2 + U_1 + U_2$ and energies of 3-electronic states are $E_{\rm III} = \frac{1}{2}(3\varepsilon_1 + 3\varepsilon_2 + U_1 + U + 2) \pm \frac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2 + U_1 - U_2)^2 + 4T^2}$. Consequently, the splitted peaks positions are $eV = \frac{1}{2}(\varepsilon_1 + \varepsilon_2 + U_1 + U + 2) \pm \frac{1}{2}\sqrt{(\varepsilon_1 - \varepsilon_2 + U_1 - U_2)^2 + 4T^2}$. As analysis for ad-atoms with different energy levels will give cumbersome expressions let us perform all the further discussion for the case of similar ad-atoms, consequently, the following relations will take place $\varepsilon_1 = \varepsilon_2 = \varepsilon_0$ and $U_1 = U_2 = U$. In this case the splitted peaks positions are $eV = \varepsilon_0 + U \pm T$. In the vicinity of the peak which corresponds to the transitions between one-electronic states and state with zero electrons in the case when measurements were performed above the single ad-atom (blue line) in the case of measurements above the coupled ad-atoms (red line) one can resolve three peaks. These peaks correspond to the transitions between 3-electronic states and 2-electronic states and between 2-electronic states and 1-electronic states. The peak with the highest amplitude is the result of both transitions $E_{\rm III} - E_{\rm II}^{\rm symm} = \varepsilon_0 + T + U/2 - \sqrt{U^2/4 + 4T^2} \simeq \varepsilon_0 + T - T^2/4U$ and $E_{\rm II}^{\rm symm} - E_{\rm I}^{\rm symm} = E_{\rm III} - E_{\rm II}^{\rm symm}$. For reasonable values of system parameters $T/U \sim 1/4$ this peak position coincides well with the position of the peak at $eV = \varepsilon_0$, revealed in the case of one ad-atom on the Ge (111) 2×1 surface (see the blue line). Two peaks with smaller amplitudes correspond to the transitions between 1-electronic states and state without electrons and 2-electronic states and 1-electronic states. One of them is visible at the values of applied bias $eV = \varepsilon_0 - T$ and another one at $eV = E_{\rm II}^{\rm symm} - E_{\rm I}^{\rm asymm} = \varepsilon_0 - T + U/2 - \sqrt{U^2/4 + 4T^2}$. We have to stress that peak which corresponds to the values of applied bias $eV = \varepsilon_0 + T$ is not visible due to the spin blockade effects [12].

The green line corresponds to the measurements of local tunneling conductivity above the domain wall and reveals oscillations in the conduction and valence bands. This is the manifestation of spatial oscillations in the density of states near domain boundaries at the Ge (111) 2×1 surface, which were revealed in [5].

5. Conclusion. We performed detailed investigations of the single and coupled ad-atoms on the Ge (111) 2×1 surface by means of low-temperature ultra-high vacuum scanning tunneling microscopy/spectroscopy technique. We revealed additional peculiarities in the local tunneling conductivity caused by the presence of Ge ad-atoms and domain wall. To analyze the reason for observed peculiarities formation we proposed theoretical model based on the pseudo-particle operators with constraint on the physical states. We revealed that additional peaks formation in the local tunneling conductivity is the result of transitions between the multi-electronic states caused by the presence of ad-atoms on the Ge surface. We consider such systems to be a good candidates for multi-electronic charge and spin configurations formation by means of STM/STS technique.

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