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Defects on the Si(100)-(2×1) surface: Anchoring sites of the surface polymerization reaction of In atoms

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Indium atoms are found to interact strongly with the so-called C defects, commonly present on the Si(100)-2×1 surface. As a consequence, In rows growing on the surface are pinned to these defects. The reaction of adsorbate with the C defects is studied in detail by *ab initio* calculations in combination with the scanning tunneling microscopy and spectroscopy. For calculations, we successfully adopted a model of the C defect as a dissociated water molecule. The presence of the defect induces a surface state just below the Fermi level, resulting in a surface-mediated reaction forming a row of indium atoms. The end of the row not pinned to a C defect is unstable at room temperature. Transition between metallic and nonmetallic characters of the unpinned termination, given by parity of atoms in the row, was observed and explained by *ab initio* calculations.

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Studying physics of low-dimensional structures and utilization of their new and unique features is a challenge of recent material research. Technique of scanning tunneling microscopy (STM) and spectroscopy (STS) can provide data important for deeper understanding of relation between atomic arrangement and electronic structure on solid state surfaces. Room temperature (RT) growth of metal rows on the Si(100)-2×1 surface is generally studied as a model system showing spontaneous one-dimensional organization. The Si(100) surface reconstructs by forming dimers aligned in rows perpendicular to dimer bonds. These dimers are buckled at low temperature, forming the $c(4\times2)$ reconstruction, while at RT, fast flip-flop motion of the dimers results in the 2×1 symmetry. Anisotropic character of the surface is responsible for one-dimensional growth of many materials, such as group III-IV metals (Al, Ga, In, Pb, Sn).[1–5] Atomic rows of group III metals are composed of dimers [Fig. 1(b)], structure of which saturates all valence electrons of the atoms involved (one electron per silicon atom and three electrons of group III atom), without causing significant stress. Mechanism of formation of the rows has been explained in the case of Al by an *ab initio* study—an increased local density of states (LDOS) in a position neighboring to a dimerized end of the row results in preferred adsorption at this site.[6] Attachment of another metal atom results in formation of a dimer again. Repetition of these two steps leads to growth of one-dimensional rows.[6] Because of its analogy in organic chemistry, Brocks *et al.* assigned this mechanism as a surface polymerization reaction.[6]

Three types of defects are commonly observed on the Si(100)-2×1 surface: A- and B-type, believed to be one and two missing dimers, respectively, and particularly interesting C-type defects.[7] Hossain *et al.* and Okano and Oshiyama independently interpreted the C defect as a dissociated H_2O molecule, with the H and hydroxyl group bonded to neighboring Si atoms of two adjacent surface dimers.[8,9] It should be noted that all experimentally observed features have not been yet satisfactorily explained. For growth of metal rows on the Si(100)-2×1 surface, the C defects play a significant role.[10,11] In contrast to previous assumptions, we found that In rows are pinned almost exclusively to the C defects. Unlike A- and B-type defects, inert to diffusing atoms, the C defects are reactive and act as nucleation centers on terraces.[10,11] An impact of neglecting the influence of the C defects is a subject of recent discussion.[10,12,13] We study in detail a mechanism of stabilization of In rows by the C de-

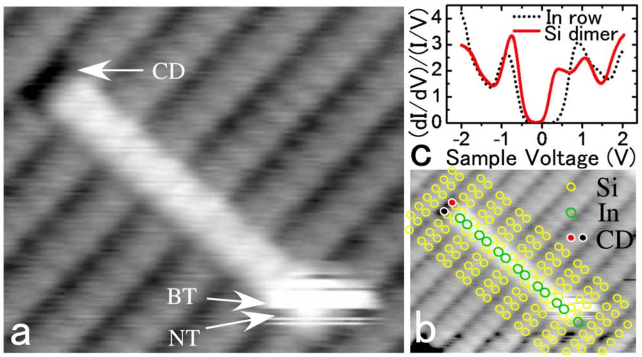

FIG. 1. (Color online) (a) STM image of the indium row anchored by the C defect (marked CD). The opposite end fluctuates between the bright and normal termination (marked BT and NT), the change corresponds to the process of single atom detachment and attachment. Scanning in horizontal direction with rate of 180 ms per line, with sample voltage of −2 V. (b) STM image shown in (a), with a proposed structural model overlaid. (c) STS spectrum proportional to a local density of states, measured at a position of In dimer within a row. A nonmetallic character is clearly revealed. As a reference, STS spectrum taken with the same tip on the clean Si(100)-2×1 surface is shown as well. The spectra are averaged from approximately ten measured characteristics. Recording time of a single spectrum was 11 s and set-point sample voltage and tunneling current where 2 V and 0.6 nA, respectively.

fects using *ab initio* calculations in combination with STM and STS.

For experiments, we used a noncommercial ultrahigh vacuum STM with a base pressure of below 2×10^{-9} Pa. Indium was deposited on Si samples (Sb doped, resistivity of $<0.014\ \Omega\,\text{cm}$) at RT directly during scanning the surface using STM. This method allows examining the surface before, during, and after deposition (*in vivo* STM). Details are described elsewhere.[14] The 2000-point $dI/dV-V$ characteristics were measured at an open control loop using lock-in detection (EG&G 5209) of the ac driven by 963 Hz, 70 mV signal added to tunneling bias.

The *ab initio* structural calculations presented in this Brief Report are based on the density functional theory and the use of the local orbital basis[15,16] (code FIREBALL). In this approach, the wave functions of valence electrons were constructed using the pseudoatomic, slightly excited orbitals,[17,18] which were confined to the regions limited by optimized radii. The ion cores were simulated by norm-conserving pseudopotentials,[19] while the exchange-correlation contributions were introduced by local-density approximation. Our total energy calculations presented here have been performed for the system where the silicon substrate was described by an asymmetric slab built up of four atomic layers: the positions of atoms in the bottom were fixed and the dangling bonds at this layer were saturated by hydrogen atoms. However, we have also performed the checking structural calculations with the silicon substrate represented by six atomic layers. The relaxation of atomic positions has been performed using the combination of conjugate gradient and dynamical quenching algorithms. Results presented in this Brief Report have been obtained for a 8×6 unit cell (if not stated else) with the use of two k points. Error of the calculated adsorption energies is estimated as <0.01 eV. Energy scale of shown LDOS spectra is related to the Fermi level.

STM simulations presented in this Brief Report were based on the nonequilibrium Green-function formalism developed by Keldysh[20] and described in detail in Ref. 21. The matrices of the Green functions and density of states which are necessary for the calculations of the tunneling current have been obtained from the local orbital Hamiltonian (sample) and the cluster-Bethe-lattice method (tip).[22] Hopping interactions between the tip and the sample were calculated using the Bardeen expression for the tunneling current between orbitals of particular atoms of the tip and the sample.[23]

In order to determine the atomic structure of In rows, the *in vivo* experimental setup allowing observation of growth directly during deposition was used. The experiment clearly showed that most of In rows are pinned to C defects. An example of the In row pinned to a C defect is shown in Fig. 1(a). From dynamical study of time evolution of the indium rows,[11] we proposed a structural model shown in Fig. 1(b). The row termination at the C defect is very stable during growth and relaxation and appears as a depression in STM images. The opposite termination fluctuates at RT due to attachment and detachment of metal atoms. At occupied states, two different terminations of the fluctuating end are observed. The bright termination (BT) or normal termination (NT) corresponds to a single indium atom or dimer, respectively.

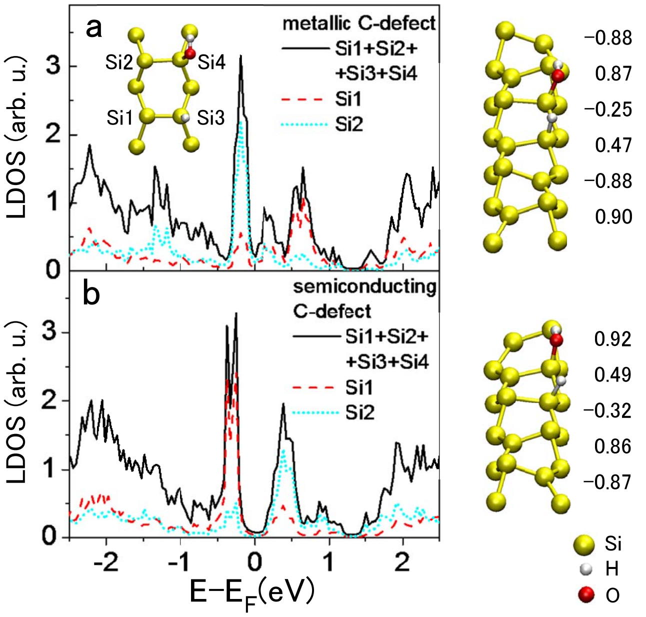

FIG. 2. (Color online) Calculated local density of states of C defects on Si(100)-2×1: (a) metallic and (b) semiconducting C defect. Atoms in Si dimers are labeled accordingly to inset in (a). Corresponding relaxed structures in top-side view are shown on right-hand side. Indicated numbers—differences in z coordinate (in Å) of atoms forming topmost Si dimers—demonstrate different bucklings.

For *ab initio* calculations, we adopted the structural model of a C defect as a dissociated water molecule.[8,9] At low temperature, Hata *et al.* observed two types of the C defects—buckling angels of the nearest unperturbed Si dimers have the same sign in one case (showing semiconducting STS spectra, therefore called semiconducting C defect) and the opposite sign in the other one (called metallic C defect).[24] These two types could not be distinguished at RT. Therefore, we tested both metallic and semiconducting case in our calculations. For calculation of the metallic and semiconducting C defect, 2×6 and 2×5 supercells were used, respectively. Stabilized structures of the both types are shown in Fig. 2 together with corresponding LDOS spectra. The density of electronic states is in a very good agreement with the low-temperature STS data measured by Hata *et al.*[24] The surface state present just below the Fermi level, localized mostly in the position of a Si atom marked Si2 in Fig. 2(a) in the case of metallic C defect) or Si1 (in the case of semiconducting C defect) is of special importance. In analogy to the surface polymerization reaction,[6] deposited metal atoms are supposed to be sensitive to this state, which results in preferred adsorption in the position next to the C defect.

The structural model of an In row as a chain of dimerized atoms pinned to a C defect [see Fig. 1(b)] was used in our calculations, starting with the C defect and one adsorbed metal atom, followed by forming a row of increasing length. To evaluate the stabilizing effect of the defects, calculations for corresponding structures on clean surface were performed. According to the calculations, the adsorption energies of an In adatom pinned to the metallic and semiconduct-

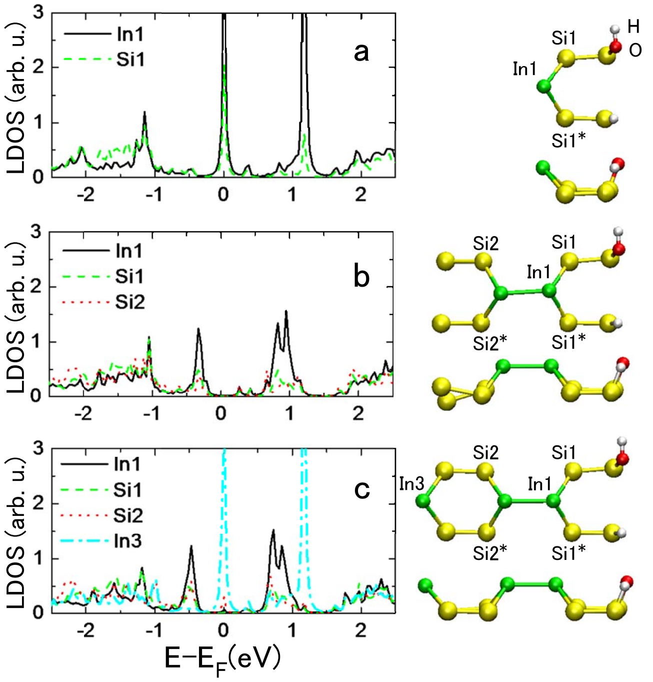

FIG. 3. (Color online) Calculated local density of states for In row growing from the position of the C defect: (a) monomer, (b) dimer, and (c) three atoms. Corresponding relaxed atomic structures (top and side views) are shown on the right-hand side panels. Locations of the spectra in (a)–(c) are marked accordingly in the structural models. The LDOSs at positions of atoms labeled Si1* and Si2* (not shown) are almost the same as the LDOS of its counterparts, Si1 and Si2, respectively.

ing C defects are 3.12 and 3.01 eV, respectively. The adsorption energy of the In atom in a corresponding position on the clean surface is much lower—2.56 eV. Therefore, both metallic and semiconducting C defects create preferred adsorption positions. From here on, we show only results obtained using the metallic C defect. However, very similar results were obtained for the case of the semiconducting defect as well. The LDOS calculated for representative positions in the case of a single In adatom pinned to the C defect is shown in Fig. 3(a). Evidently, the presence of the In adsorbate changes significantly the electronic structure of the considered system [compare to LDOS of the C defect shown in Fig. 2(a)]. Now, LDOSs at the position of an In and two nearest Si atoms exhibit a sharp maximum located at the Fermi level—the system is strongly metallic.

We continue by calculation of two In atoms on the surface. A metal dimer pinned to the C defect represents the most stable structure examined—the adsorption energy of the second In atom is 3.74 eV. The relaxed structure is shown in Fig. 3(b). The pinned indium dimer is more stable than a dimer adsorbed on the clean surface—the corresponding energy difference is 0.17 eV. The presence of the second atom changes again the electronic structure of the system significantly, as shown in Fig. 3(b). The LDOS maximum present at the Fermi level in the case of a monomer now disappears and the electronic structure of the whole system becomes nonmetallic.

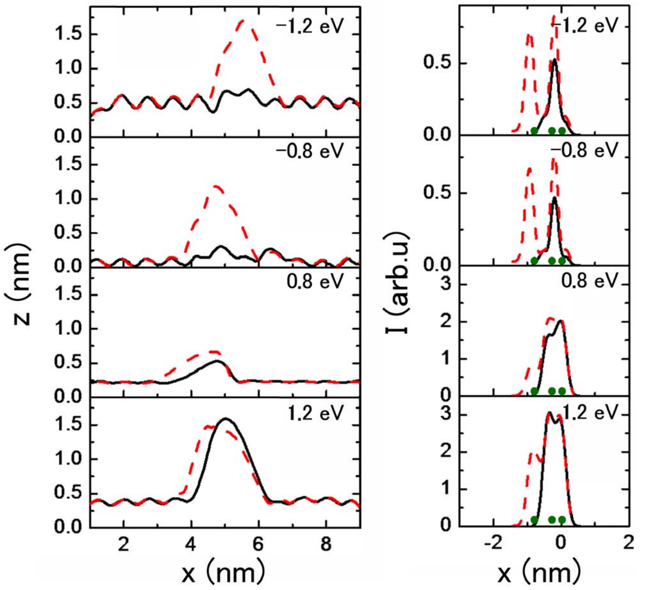

FIG. 4. (Color online) STM profiles along the row formed by two (solid line) and three (dashed line) indium atoms obtained at various sample voltages, as indicated in each frame. Left panel—measured profiles (constant current mode); right panel—calculated profiles (constant height mode). The circles show lateral positions of the In atoms in the case of calculated profiles.

Adding further In atoms to the row gives results similar to those obtained for the monomer and dimer pinned to a C defect. The electronic structure of the row termination shows repeatedly the metallic or nonmetallic character according to the termination by a single atom or dimer, respectively. The adsorption energies of third to sixth atoms terminating the row are 2.86, 3.74, 2.87, and 3.73 eV, respectively.

The *ab initio* calculations show that electronic structure and stability of the last atom in a row strongly depend on parity of number of indium atoms in the row (Fig. 3). In the case of an odd number, the last atom is not dimerized and one of the three valence electrons of the In atom is not paired. This half-filled surface state results in metallic character of LDOS in the positions of the last In atom and two nearest Si atoms. The difference in electronic structure can be resolved by STM. Figure 4 shows both measured and calculated STM profiles along the rows formed by two and three atoms. A direct comparison of profiles is difficult, due to many factors, such as different imaging modes and different shapes of STM tips. Nevertheless, the relevant features agree: The row composed of three atoms appears much brighter than a dimer; the effect is stronger especially at occupied states. This big difference in contrast explains well the switching between bright and normal terminations, as shown in Fig. 1(a). Hence, the bright and normal terminations correspond to termination by the monomer and dimer, respectively.

Nonmetallicity of dimerized In atoms was proofed by means of scanning tunneling spectroscopy [Fig. 1(c)]. The absence of states at the Fermi level is clearly consistent with the calculated LDOS spectra. Unfortunately, the terminations by single indium atoms are too unstable at RT for reliable STS measurement.

With respect to the calculated stabilizing effect of the C defects, we propose the following scenario for growth of metal rows on the Si(100)-2×1 surface. Deposited atoms migrate on the surface, until they attach to C defects or another metal atoms. The atoms tend to align to one-dimensional rows due to their anisotropic surface-mediated interaction. Rows unpinned to C defects are unstable; with time, the most stable terminations—at C defects—dominate. Therefore, in a dynamic equilibrium, all In rows on the surface are anchored at the C defects. The time necessary to reach the dynamic equilibrium depends on strength of bonding within metal rows and can vary for different metals.

In conclusion, interaction between the C defects and metal adsorbate on silicon surface was studied by *ab initio* calculations. We show the anchoring effect of the C defects, commonly observed on the Si(100)-2×1 surface, for growth of the In rows. The model of the C defect as a dissociated water molecule satisfies well the experimentally observed features. The presence of the C defect results in the surface state just under the Fermi level. Indium adatoms are sensitive to this surface state; bonding at this position is stronger by 0.5 eV in comparison with the equivalent position on the clean silicon surface. Adsorption of the second In atom—formation of a dimer—results in the even more stabilized structure. Adding or removing of a single atom results in changing electronic character of the row end; structures terminated by the monomer or dimer have strongly metallic or nonmetallic character, respectively. This feature was revealed by STM observations as well. A similar behavior can be expected in the case of other group III metals deposited on the Si(100)-2×1 surface.

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