Theoretical Simulations of 0.25 Monolayer Iodine Adsorption on Cu(100)

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Simulations of adsorption 0.25 monolayer of iodine on Cu(100) were performed using a local-orbital minimal basis technique based on density functional theory and compared with plane-wave basis results. It was found that iodine adsorption changes the spacings between surface layers of copper substrate and can cause the reconstruction of this surface to rhombus-like arrangement with a stable threefold hollow adsorption site. The calculated structure of I/Cu(100) is presented together with the simulated scanning tunneling microscopy images of this surface. The obtained results are discussed in comparison with experimental results.

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1. Introduction

The halide adsorption on the Cu surfaces is interesting because of the understanding of catalytic processes, in vacuum and in solutions. Iodine adsorption on Cu(100) surface is of interest as a peculiar case of halogen adsorption on metal surface. For this surface, the surface corrugation potential is known to be stronger than for the (111) surface [1], which is expected to influence the adsorbate layer structure. On the another hand, the iodine adsorption on a copper surface presents an example of large-atom adsorption on a metal surface with a small lattice constant, similarly to a iodine adsorption on nickel surface. This is why the 0.25 monolayer of adsorbate seems to be the highest coverage forming the regular structure on Cu(100). When still higher coverages of iodine are adsorbed, the incommensurate structures of adsorbate are expected [2, 3]. This concerns even c(2×2)-I phases on Cu(100) and Ni(100) [3]. The commensurate p(2×2) structure of iodine on Cu(100) surface was observed by means of X-ray absorption [4] and low energy electron diffraction (LEED) [5] investigations. In more detail, the iodine adsorption on Cu(100) was studied by Andryushechkin et al. [3] by

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means of LEED and scanning tunneling microscopy (STM) under ultrahigh vacuum conditions. At low coverages, the c(14×2), c(6×2), c(5×2) structures have been observed. The most dense regular structure was p(2 × 2) for the coverage of 0.25 monolayer. For higher coverages, a disordered phase characterized by a diffuse pattern was found.

Theoretically, the iodine adsorption was investigated on a variety of Cu surfaces (from (100) to (643)) using density functional technique and plane wave basis (VASP package) [6]. For the p(2 × 2)-I phase on Cu(001) surface, the expected high-symmetry adsorption sites have been examined. The hollow position was found to be energetically most favorable.

Here we simulate adsorption of the 0.25 monolayer of iodine on the Cu(100). The influence of adsorbate on the surface structure is examined in detail. Calculated STM images of the resulting surface structure are presented.

2. Method of calculation

The calculations have been performed using a local-orbital minimal basis technique based on density functional theory (DFT) [7, 8]. The code Fireball 2005 has been used [9, 10], where ion cores are simulated by norm-conserving pseudopotentials [11]. The FHI-98PP package has been used to construct pseudopotentials [12] within the scheme of Troullier and Martin [13] while the exchange-correlation contributions are introduced by local density approximation. The absence of unphysical states has been checked by inspection of the bond state spectrum and by analysis of Gonze et al. [14]. The pseudopotentials are transformed into the fully separable form of Kleinman and Bylander [15].

The local-orbital basis MD-DFT (Molecular Dynamics based on the DFT) approach has been applied to find the minimum-total-energy atomic configuration. In this kind of calculations atomic orbitals are confined to the regions limited by the corresponding atomic-orbital radii. As it has been found, the best choice is to confine copper orbitals to $R_c(\mathrm{Cu},s^1) = 4.2$ a.u., $R_c(\mathrm{Cu},p^0) = 4.6$ a.u. and $R_c(\mathrm{Cu},d^{10}) = 3.5$ a.u. Such a choice results in a lattice constant of 3.63 Å and a bulk modulus of 182 GPa, whereas experimental values are 3.61 Å and 142 GPa, respectively [16]. The iodine orbital radii are taken to be $R_c(\mathrm{I},s^2) = 7.1$ a.u. and $R_c(\mathrm{I},p^5) = 4.9$ a.u., to reproduce the length of Cu–I molecular bond of 2.338 Å [4].

Surface properties of the I/Cu system have been computed for seven-layer Cu slab with the p(2 × 2) surface cell using dynamical quenching method. The supercell contains 28 Cu atoms and 2 I atoms, one at every surface of this slab. All layers of the copper and iodine atoms have been allowed to relax. For comparison, the calculations have been repeated using plane-wave basis technique based on the density functional theory (VASP package) [17–20]. In plane-wave calculations electron exchange-correlation effects have been described via the generalized gradient approximation (GGA) using the Perdew–Wang functional. A plane-wave cut-off of 270 eV was used in all calculations. Within this method, the lattice constant of

3.63 Å and bulk modulus of 138 GPa have been received. The geometry of (100) oriented slab was relaxed using a quasi-Newton algorithm. A Monkhorst–Pack mesh with a $9 \times 9 \times 1$ k-grid have been used for the slab.

Simulations of STM images are based on the non-equilibrium Green-function formalism [21]. Calculations of the tunneling current are performed for a tungsten tip, formed by 5-atoms pyramid connected to (001) oriented tungsten slab. Electronic structure of the tip and hopping interactions between the tip and the substrate have been calculated within the Fireball2005 formalism. The local orbital radii chosen for bulk tungsten are: $R_c(W,s^2) = 5.60$ a.u., $R_c(W,p^0) = 4.60$ a.u., and $R_c(W,d^4) = 5.08$ a.u. Such a choice yields the bulk W lattice constant of 3.165 Å and bulk modulus of 315 GPa. The hopping interactions between W–I and W–Cu have been determined using the local orbital radii of 12 Å for all kinds of atoms, as there is no reason to account for any screening effects in such cases. The hopping interactions have been analytically extrapolated for distances, for which results obtained from Fireball package become unstable (i.e., distances bigger than 7 Å).

All presented STM images have been simulated in a constant-height mode. The sample bias equals to –2.0 eV.

3. Results

First, the clean Cu(100) slabs of 5, 7, 9, and 11 atomic layers have been relaxed, indicating that it is sufficient to consider a seven-layer slab in the calculations. Interlayer relaxations $\Delta_{ij} = d_{ij} - d$, between layers i and j with respect to the bulk spacing $d = 1.81$ Å, are equal to: $\Delta_{12} = -0.2\%$ and $\Delta_{23} = +1.3\%$ for the topmost layers. Experimental values are between -1.2% and -3.79% for Δ_{12}, and between 0.9% and 1.0% for Δ_{23} [22]. Calculated values given in [22] are –3.02% for Δ_{12} and 0.08% for Δ_{23}.

Next, the Cu(100) slab covered with 0.25 monolayer of iodine has been investigated. There are expected three high-symmetry adsorption sites for iodine atoms on Cu(100) surface at low coverage, namely fourfold hollow, the twofold bridge, and the on-top site. Such favorable configurations have been relaxed in the framework of Fireball scheme, using dynamical quenching method with temperature of the start of 400 K.

As a result, none of them appeared to survive and new minimum energy configuration of I/Cu(100) surface has been found. The first layer of copper atoms reconstructed to a rhombus-like shape (Fig. 1). Also values of Δ_{ij} changed: $\Delta_{12} = +14\%$, and $\Delta_{23} = +2\%$. The Cu–I distance equals 2.62 Å. The found adsorption site appears to be threefold coordinated. The energy of found configuration is 0.02 eV favorable to the fourfold hollow one per surface cell (the last energy value is estimated by relaxing the slab in direction perpendicular to the surface with coordinates of atoms artificially fixed in directions parallel to the surface). Calculations performed with the use of VASP package confirmed the

surface structure discussed above to be a minimum total energy configuration, but by 1.45 eV per p(2 × 2) surface cell less favorable than the surface configuration without Cu surface reconstruction and with adsorbate atom in the hollow site.
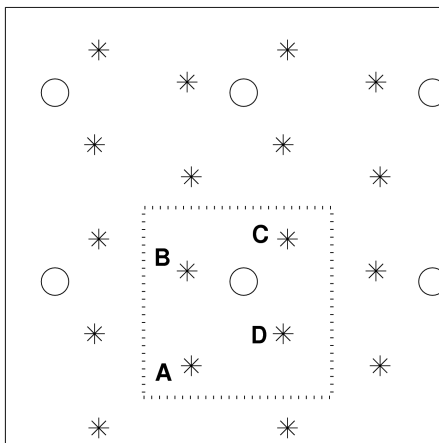

Fig. 1.   The I/Cu(100)-p(2 × 2) surface. Iodine atoms are marked by open circles and copper atoms are marked by stars. Surface cell is marked with dashed line. Distances between Cu atoms in the first layer are equal to 2.58 Å for BC and CD and 2.87 Å for AB and AD.

The simulated STM images for the found configuration of adsorbed surface done for two tip sample distances of 5 Å and 7 Å above iodine adsorbate atoms are qualitatively the same. These images (Figs. 2 and 3) show that the bright spots are connected with iodine atoms. Besides, it can be seen that the spots corresponding to iodine atoms build bright stripes, in spite the adsorbate itself forms square lattice. Similar stripes appear in the STM measurements [3]. The bright protrusions in the image of atomic configuration with fourfold coordinated hollow adsorption sites cannot be connected in stripes. We interpret appearance of these stripes as a result of the copper substrate reconstruction to rhombus-like shape.

4. Conclusions

Adsorption of 0.25 monolayer of iodine on p(2 × 2)-Cu(100) surface has been studied using the *ab initio* local orbital method based on DFT. The STM images of found minimum total energy structure have been simulated. The conclusions are summarized as follows:

- Iodine adsorption changes the spacings between surface layers of copper substrate and can cause the reconstruction of this surface to rhombus-like arrangement.
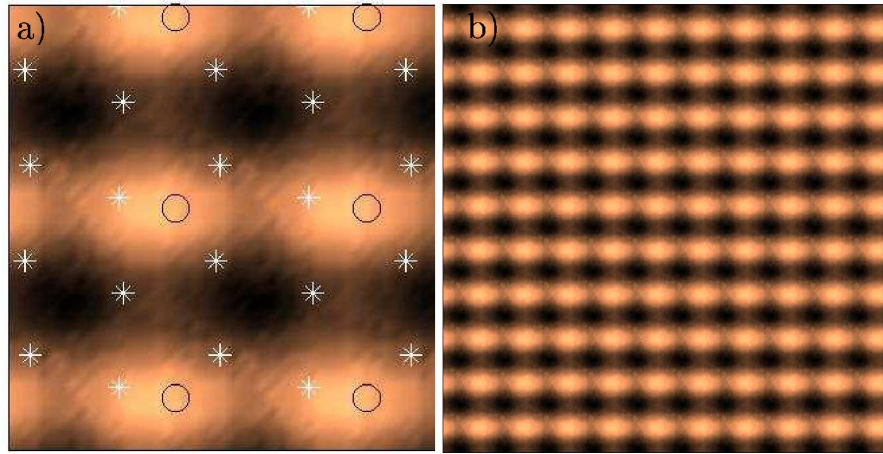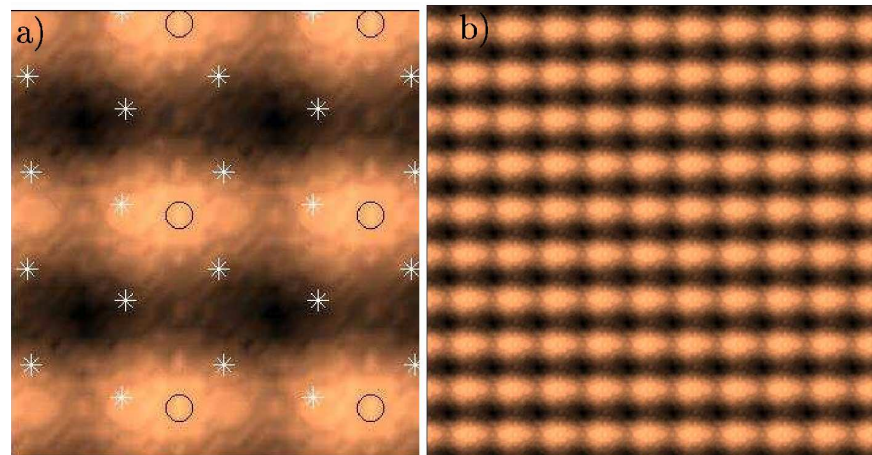
Fig. 2. Simulated STM images for the I/Cu(100)-p(2×2) surface structure presented in Fig. 1. The tip–sample distance of 5 Å (above adsorbate atoms): (a) scanning area 12 Å $\times$ 12 Å — iodine atoms are marked by open circles and copper atoms are marked by stars. (b) scanning area 50 Å $\times$ 50 Å.

Fig. 3. Simulated STM images for the I/Cu(100)-p(2×2) surface structure presented in Fig. 1. The tip–sample distance of 7 Å above adsorbate atoms: (a) scanning area 12 Å $\times$ 12 Å — iodine atoms are marked by open circles and copper atoms are marked by stars, (b) scanning area 50 Å $\times$ 50 Å.

- The stable threefold hollow adsorption site has been found.

- The simulated STM images present bright spots, corresponding to adsorbate atoms, connected into stripes. Such stripes are similar to these observed in STM measurements [3]. Appearance of the stripes can be connected with rhombus-like shape reconstruction of the substrate surface layer.

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