Coexistence of two diffusion mechanisms: W on W(100)

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We utilized the field ion microscope and density functional theory to investigate surface diffusion and surface adsorption of W on W(100). We demonstrated experimental proof for the occurrence of the exchange diffusion mechanism on W(100) and its coexistence with adatom jump. From our study it is evident that the primary mechanism of motion is atom exchange which is activated on the time scale of seconds at a temperature of around 650 K and is associated with an activation energy of 1.6 eV. Additionally, at a temperature around 700 K we observe a second surface diffusion mechanism with the activation energy estimated as ∼2.1 eV, which we associate with adatom jump. Our findings are in excellent agreement with DFT investigations. We have performed the adsorption-desorption experiments as a method helping with determining the morphology of a W(100) surface.

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Surface diffusion is a central process of nanotechnology. To model processes and devices in nanoscale it is crucial to know the mechanism and the energetics associated with the basic steps of adatom motion. Presented in 2012 by Fuechsle *et al.* [1] a single atom transistor shows how important is understanding and controlling the behavior of single atoms migrating on the surface. In this study the final stage of device preparation is achieved by embedding a phosphorus adatom in the silicon matrix via exchange mechanism.

The morphology of the surface plays an important role in surface diffusion since it can affect the adatom's diffusion mechanism. For many years the arrangement of surface atoms on W(100) has been a subject of intense debate. The low energy electron diffraction (LEED) measurements conducted by Felter *et al.* [2] discovered that below 300 K the surface undergoes a reversible transition from a bcc(100) bulklike (1×1) structure to a structure with a $c(2 \times 2)$ LEED pattern. Felter, Barker, and Estrup [2] explained the occurrence of additional $(1/2, 1/2)$ LEED peaks as a vertical shift of every second surface atom, and we called it the FBE model. Debe and King [3] analyzed the intensity of electron peak spectra in the LEED pattern and noticed twofold symmetry. They proposed an alternative model of W(100) surface called "zigzag" model, in which atoms are laterally displaced along the [110] direction. Later this displacement was found to be 0.15–0.3 Å [4]. The zigzag model was supported by investigations of various groups conducting LEED and scanning tunneling microscopy (STM) experiments [5] and first-principle calculations [6]. The field ion microscopy (FIM) experiments done by Tung *et al.* [7,8] as well as Tsong and Sweeney [9] did not show a zigzag. Additionally Tung *et al.* [7,8] noticed that on W(100) the atoms adjacent to the step edge desorb earlier than atoms of the step edge which argues against ordinary field evaporation. The abnormal behavior of W(100) during field evaporation and $c(2 \times 2)$ arrangements of very small clusters (16–19 atoms) suggested the validity of the FBE model. Tsong and Sweeney [9] investigated small planes (∼50 atoms) of W(100) with FIM and at 20 K they resolved (1×1) atomic arrangement questioning both reconstructions. They did not explain the effect of odd field evaporation on W(100) leaving the problem as an open question. Nishikawa *et al.* [10] investigated the structure of W(100) utilizing FIM and covering the surface with a layer of Ga and Sn. They analyzed the adsorbate arrangement on W(100) right after deposition and during slow field evaporation. The Sn layer creates a (1×1) structure but the arrangement changes during field evaporation to $c(2 \times 2)$. A surface covered with Ga keeps the (1×1) arrangement during adsorption as well as during field evaporation. Behavior of Ga layer on W(100) was interpreted as a proof of flaw of the FBE model. They did not observe the zigzag directly, but assigned abnormal field evaporation to this model.

The surface diffusion on open W(100) was experimentally investigated with FIM for nickel adatoms by Kellogg [11]. However, their study did not include the effects of diffusion mechanisms. The mechanism of adatom migration on W(100) was investigated in the framework of theoretical study based on the first-principles calculations [12,13] where the motion of iron and manganese was explored on an unreconstructed and zigzag reconstructed plane. For both adsorbates, the leading mechanism on both types of surfaces was found to be an adatom jump. The self-diffusion on the unreconstructed W(100) surface was first investigated by Flahive and Graham [14] using the Morse potential. In their research, only the jump mechanism was taken into account. Recently, Chen and Ghoniem [15] used the more reliable VASP and found the crowdion as a leading mechanism of motion. We investigated the mechanism and energetics of a tungsten atom diffusing on a W(100) surface using FIM. We carried out density functional theory (DFT) calculations on unreconstructed and zigzag reconstructed surfaces. The FBE model of the surface has not been considered in our study because our DFT calculations show that this structure seems to be unstable. In our work the mechanism of motion, energetics, and information about surface morphology were determined.

The field ion microscope with helium as an imaging gas allows one to accurately resolve the positions of adatoms and edge atoms of the surface. Even though it is not possible to

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image directly the interiors of large planes, the morphology of the surface can be deduced via analysis of the arrangement of the adsorption sites for the adatom. In our experiments, tungsten and rhodium adatoms were used to mark positions of adsorption sites. The sample was a sharp tip ~154 Å in radius that was made by electrochemically etching a ⟨100⟩ oriented tungsten wire in 2N NaOH. The final stage of preparation of the sample was done by field evaporation of the tip in the FIM chamber. A central W(100) plane, used in the experiment, was ~45 Å in diameter. The experiment was conducted in ultrahigh vacuum conditions: the base pressure was $p_0 = 10^{-11}$ Torr and the pressure of helium gas during the imaging process was $p_{\mathrm{He}} = 10^{-4}$ Torr. During field evaporation and imaging processes, the tip was kept at a temperature ~20 K.

The theoretical part of our study is based on the *ab initio* structural calculations performed with the use of DFT as it is implemented in VASP code [16–19] with a plane wave basis set. The description of the electron-ion interactions has been performed in the framework of the projector-augmented wave (PAW) method. The exchange-correlation contributions were included using generalized gradient approximation (GGA) in its PW91 formulation. The Davison-Block algorithm has been applied to obtain the convergence of the energy of electronic states [20], while the atomic structure has been relaxed using the conjugate gradient approach. The lattice constant obtained from the energy optimum condition of the bulk unit cell equals 3.175 Å. In all calculations the W(100) substrate was simulated by the asymmetric slab composed of seven atomic layers where the atoms from the topmost four planes were allowed to relax while the rest of the system was frozen in its bulklike configuration. Because of the asymmetry of the slab, the dipole correction has been introduced. To determine the activation barriers for the diffusion of a tungsten adatom, the 4 × 4 surface unit cell was applied. Simulations of the exchange-diffusion process have been performed with the use of the nudged elastic band method (NEB) implemented in VASP code [21–23]. The surface structures of W(100) substrate with zigzag reconstruction and unreconstructed obtained from our structural calculations are shown in Fig. 1. We find that in the zigzag structure the topmost atoms are shifted laterally by 0.27 Å with respect to the square lattice. This result remains in a perfect agreement with the corresponding value obtained in earlier theoretical work [12]. Atoms from the topmost layer

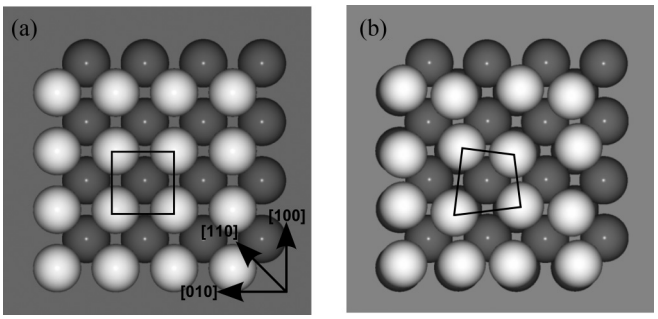

FIG. 1. Top view of the positions of W(100) surface atoms obtained from DFT calculations for (a) an unreconstructed and (b) a zigzag reconstructed surface.

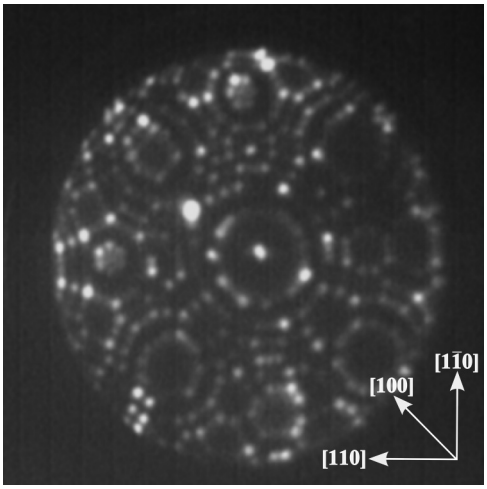

FIG. 2. FIM picture of a whole tip with a central W(100) plane and with an adsorbed adatom.

are located vertically on the same level (no vertical shifts of atoms within the layer).

The experiment cycle of the FIM measurements was as follows: A single atom (W or Rh) was deposited from a hot filament onto a clean W(100) surface kept at 20 K. Then, a high voltage ~8 kV was applied between the tip and the screen to resolve the position of the adatom. After recording the position of the adatom, shown in Fig. 2, a higher field was applied (~9 kV for Rh and ~10 kV for W) to desorb the adatom from the surface. Then, the electric field was turned off and a new adatom was deposited again to mark another adsorption site. The procedure was repeated about 25–68 times. The aim of this investigation is to understand the morphology of the surface during field free thermal diffusion. During investigation of thermal surface diffusion, the experiment is carried on in a "quench and look" routine, i.e., the motion of the adatom proceeds at temperatures above 500 K for set period of time, afterwards the surface is quenched to 20 K for imaging. Therefore, to fully understand the diffusion process we investigated the map of adsorption places of the surface kept at 20 K, as well as preheated first to 532 K for 30 s then quenched to 20 K. The map of adsorption sites is shown in Fig. 3(a) and it is the same for the surface kept at 20 K and preheated to 532 K. We compare the orientation of the grid with the position of the crystal planes surrounding the W(100) plane (Fig. 2) and determine that the grid is oriented along the ⟨100⟩ directions. For both W and Rh adatom, the arrangement of adsorption sites is (1 × 1) with respect to the surface. The diffusion proceeds at temperature above 220 K in which previous experiments [24] showed a (1 × 1) structure of W(100). The diffusion interval is followed by rapid quenching to 20 K for imaging where zigzag reconstruction might be present. Our DFT calculations indicate that the zigzag reconstruction reduces the total energy of the system. We have found that for a 4 × 4 unit cell the total energy decreases by 1.35 eV/unit cell with respect to the unreconstructed surface. This means that at 0 K the zigzag reconstruction is energetically more favorable. The lateral displacement of surface atoms on a zigzag reconstructed surface causes a

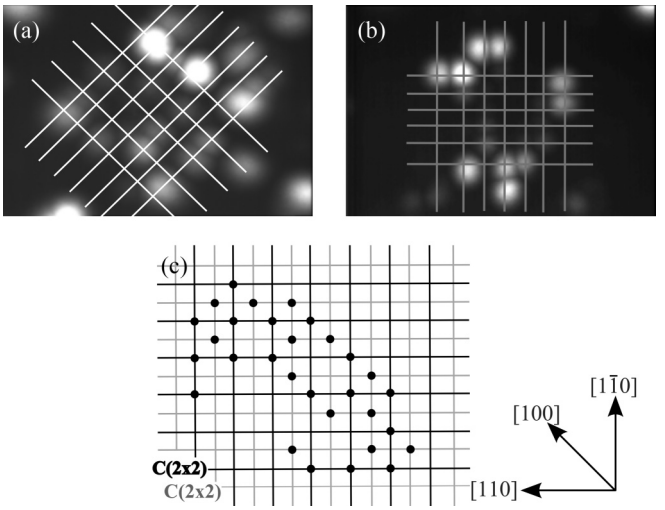

FIG. 3. Adsorption and diffusion on W(100): (a) Adsorption of Rh—stack of 25 FIM pictures with matched grid oriented along the ⟨100⟩ directions. (b) Diffusion of W—stack of 73 FIM pictures showing the position of a diffusing adatom at 700 K. Matched grid is oriented along the ⟨110⟩ directions and corresponds to a $c(2 \times 2)$ arrangement. (c) Map of the averaged positions of adatoms diffusing at 720 K, with two alternating $c(2 \times 2)$ grids.

shift in positions of adsorption places with respect to the unreconstructed surface. The adsorption places on a frozen reconstructed surface are displaced 0.12 Å with respect to each other, so the map of adsorption places should have a zigzaglike appearance. However adsorption of an adatom on the surface causes an additional local relaxation of the lattice. We looked at the positions of adatom and lattice atoms close to adatom with DFT and we found that the position of an adatom adsorbed on an unreconstructed surface is exactly the same as the position of an adatom deposited on the zigzag relaxed reconstructed surface. This is caused by a different response of the lattice atoms upon adatom adsorption. On the unreconstructed surface, all four of the closest surface atoms relax outwards 0.075 Å. On the zigzag structure, the surface atoms relax 0.08–0.19 Å creating a quasiquadratic adsorption place. Thus, the maps of adsorption places on both surfaces are exactly the same, making them undistinguishable in FIM. Even if the surface undergoes reconstruction during quenching, it does not influence the diffusion characteristic, since the adatom adsorbs exactly at the same place on the unreconstructed and reconstructed surface.

The diffusion experiments were conducted only with a tungsten adatom. When the adatom was adsorbed onto the W(100) surface, its position was recorded with FIM. After the adatom's position was marked, the electric field was turned off and the sample was heated to a temperature between 662 and 726 K for set period of time (60–5 s) allowing the adatom to diffuse. Afterwards, the sample was rapidly cooled with liquid helium to about 20 K and the electric field was applied again to record a new position of the adatom. The cycle was repeated ∼70–140 times per each temperature, until a map of sites visited by the adatom was created and the grid was matched. In Fig. 3(b) we present a stack of adatom positions seen in FIM after diffusion at 700 K. Surprisingly, the map exhibits the $c(2 \times 2)$ arrangement of positions with the grid oriented along ⟨110⟩ directions. Additionally, when we desorb an adatom and adsorb a new adatom on the same surface, it occasionally lands in an interstitial place of a previous $c(2 \times 2)$ grid and we observe it moving in an alternative $c(2 \times 2)$ map. Such a map of adsorption sites can be associated with the motion of an adatom by exchange in which the adatom incorporates into the surface, replacing one of the surface's atoms. The lattice atom is pushed to the top of the plane and continues motion [25]. It has been previously shown by Kellogg and Feibelman [26] for motion of platinum adatoms on Pt(100) surface and by Chen and Tsong for self-diffusion on Ir(100) [27] that the adatom diffusing via the exchange mechanism leaves the map of visiting sites arranged as $c(2 \times 2)$. Thus we conclude that tungsten adatoms diffuse on the W(100) surface via exchange. Due to uncertainty of the surface structure of the W(100) surface, we performed DFT calculations of exchange and jump on both unreconstructed and zigzag reconstructed surfaces. For both surfaces, DFT confirmed that the leading mechanism is adatom exchange. The energetic sequence between exchange and hopping agrees with the

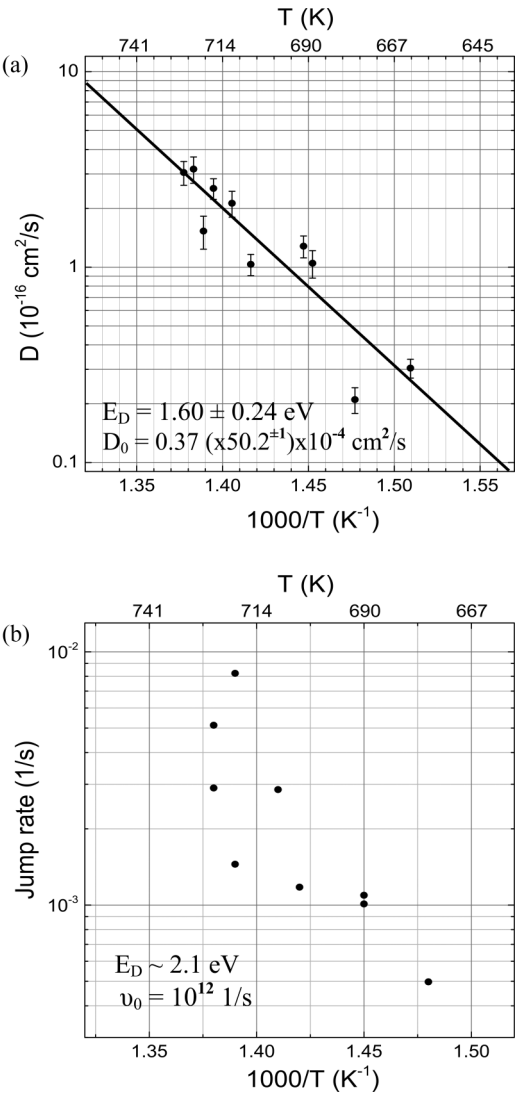

FIG. 4. Arrhenius plots for (a) diffusivity and (b) adatom jump rate.

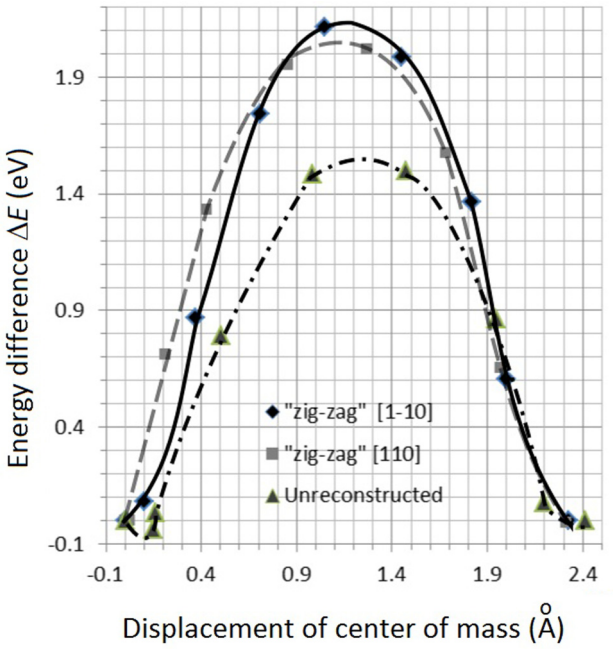

FIG. 5. (Color online) The shapes of barriers experienced by adatoms during exchange on unreconstructed and zigzag reconstructed surfaces.

previous findings of Chen and Ghoniem [15] performed on an unreconstructed surface.

Diffusivity was determined based on adatom mean squared displacement $\langle \Delta r^2 \rangle = 4Dt$ (where t is a time interval) and an Arrhenius plot constructed as shown in Fig. 4(a), which yields an activation energy of 1.60 ± 0.24 eV for an adatom exchange and a prefactor $D_0 = 0.37\ (\times 50.2^{\pm 1}) \times 10^{-4}$ cm^2/s. The data agree perfectly with the activation energy of 1.55 eV for the exchange mechanism on an unreconstructed W(100) surface, obtained from our DFT calculation, and also are in good agreement with the findings of Chen and Ghoniem [15]. The activation energy for an adatom moving via exchange on the zigzag reconstructed surface is 2.05 eV for the [110] direction and 2.11 eV for the [1−10] direction. Figure 5 presents the shape of barriers experienced by the adatom during exchange on reconstructed and unreconstructed surfaces. The change in energy of the system is plotted as a function of displacement of the center of mass adatom-displaced-surface-atom complex. Based on the agreement between the experimental value and the value obtained from DFT calculations for an unreconstructed surface, we conclude that the adatom is moving via exchange on the unreconstructed W(100) surface.

At higher temperatures we observed that the arrangement of positions visited by the adatom corresponds to a (1×1) map [Fig. 3(c)]. However, a careful inspection of the adatom's movement showed overlapping of two $c(2 \times 2)$ maps with few transitions of adatoms between two alternative $c(2 \times 2)$ maps. Since the event occurs occasionally, we have insufficient data to obtain the activation energy of the process directly. From a plot of the rate of jumps vs temperature [Fig. 4(b)] we can see that the jump rate increases with increasing temperature. Assuming a standard attempt frequency ν_0 of 10^{12} s^{-1}, we roughly estimate the activation energy for the process to be 2.1 eV. We believe that the transition between two grids is a result of the adatom's jump. We cannot ruled out completely possibility that disassembling of the crowdion could provide a similar map. Unfortunately FIM is not a suitable tool to follow crowdion motion. However, according to Chen and Ghoniem [15], the crowdion mechanism has lower activation energy than exchange, therefore the (1×1) map should be observed at lower temperature than $c(2 \times 2)$, which does not agree with the obtained experimental results. The estimated value of activation energy for an adatom jump is in good agreement with the results of our DFT calculations for adatom jumping on an unreconstructed W(100) surface, which is 2.27 eV, also agrees with the value provided by Chen and Ghoniem [15]. The calculated activation energy for adatom jump on the zigzag reconstructed surface is 2.49 eV for the short bridge and 2.48 eV for the long bridge. This once more confirms that observed motion proceeds on an unreconstructed W(100) surface. The competition of two diffusion mechanisms was previously deduced for mass diffusion by Prévot *et al.* [28] for motion of lead on Cu(110). We have provided a direct proof of coexistence of two mechanisms.

Based on our investigations we conclude that the leading mechanism for motion of W on the W(100) surface is adatom exchange, which proceeds with an activation energy of 1.6 eV. With increasing temperature, the second mechanism, identified by us as the adatom jump, starts to be present on the surface, with an activation energy of 2.1 eV. Additionally we deliver evidence that the motion of an adatom proceeds on an unreconstructed W(100) surface.

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