PHYSICAL REVIEW B **82**, 073406 (2010)

Activated O_2 dissociation and formation of oxide islands on Be(0001): An atomistic model for metal oxidation

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(Received 11 May 2010; revised manuscript received 3 August 2010; published 19 August 2010)

Based on first-principles molecular-dynamics simulations, we propose an atomistic model for the oxygen dissociation and oxide nucleation on the Be(0001) surface. In our model, only the dissociation of the initial oxygen molecule needs to overcome an energy barrier while the subsequent oxygen molecules dissociate barrierlessly around the adsorption area. Consequently, oxide islands form on the metal surface and grow up in a lateral way. We also discover that the initially dissociated oxygen atoms are not so mobile on the Be(0001) surface, as on the Al(111) surface. Our atomistic model enlarges the knowledge on metal surface oxidations by correctly explaining the initial phenomena during the surface oxidation of Be.

DOI: 10.1103/PhysRevB.82.073406 PACS number(s): 68.43.Bc, 68.43.Mn, 81.65.Mq, 71.15.Nc

Most metal surfaces are thermodynamically allowed to react with oxygen molecules in the atmosphere, to form thin oxide films.[1] This phenomenon is very important for many technological applications because they are directly relevant to surface corrosion and the formed metal oxide films have been widely used as catalysts, sensors, dielectrics, and corrosion inhibitors.[2,3] In addition, studying the oxidation reactions from the atomic view is also of great scientific importance.[4–7] However, the detailed atomistic models for the surface oxidation of metals are not yet mature.[8–11] A "hot-atom" O_2 dissociation and oxide nucleation model was recently proposed for the oxidation of the Al(111) surface, in which the dissociative adsorption of O_2 molecules occurs via a hot-atom mechanism and O atoms are spontaneously incorporated underneath the topmost Al surface layer, initiating the nucleation of the oxide far below the saturation coverage of one O adlayer.[9] However, the applicability of this model has not been checked for other metals, for example, whether the dissociated O atoms on other metal surfaces are "hot" or not is still beyond the present knowledge. Besides, there is a contradiction with experimental observations in the atomistic model. The initial sticking probability of thermal O_2 molecules at Al(111) is measured to be low by many independent experiments,[12–14] suggesting a sizeable energy barrier for the O_2 dissociation, which however is not included in the hot-atom mechanism. The lack of an energy barrier is contributed to the fact that in the adiabatic first-principles calculations the lowest unoccupied electronic state of oxygen is aligned with the Fermi level at any distance between the molecule and the surface, allowing a partial filling of the empty molecular orbital, which finally drives the dissociation.[9]

Based on this background, in this Brief Report we have carried out first-principles molecular-dynamics (FPMD) simulations for O_2 dissociation on the Be(0001) surface, which is also motivated by the fact that Be has vast technological applications due to its high melting point and low weight.[15–18] During these applications, surface oxidation as the main kind of corrosion always needs to be prevented. Experimentally, the surface oxidation of Be is reported to begin by forming separate oxide islands and saturate after the islands grow laterally together forming an oxide layer.[15–17] Theoretically, we have calculated the adsorption properties of O_2 molecules on the Be(0001) surface,[19] and identified both the physisorbed and chemisorbed molecular precursor states. Remarkably, we have revealed that unlike the Al(111) surface, the alignment of the lowest unoccupied electronic state of oxygen with the Fermi level does not happen when it is in close with the Be(0001) surface.[19] Therefore, the Be(0001) surface is in some way a better model system for studying the metal oxidation using adiabatic first-principles methods.

Our calculations are performed using the spin-polarized version of the Vienna *ab initio* simulation package.[20] The PW91 (Ref. 21) generalized gradient approximation and the projector-augmented wave potential[22] are employed to describe the exchange-correlation energy and the electron-ion interaction, respectively. The cut-off energy for the plane-wave expansion is set to 400 eV. The molecular-dynamics (MD) simulations are performed using the Verlet algorithm with a time step of 1 fs within the micro canonical ensemble. The Kerker mixing scheme[23] is employed for charge density optimizations. In our present study, the Be(0001) surface is modeled by a periodically repeated slab of five Be layers separated by a vacuum region correspondent to six metal layers. We consider a (4×4) surface unit cell, which includes 16 Be atoms in each atomic layer. The surface Brillouin zone is sampled by a 3×3 k-point distribution using the Monkhorst-Pack scheme.[24] The calculated lattice constant of bulk Be (a,c) and the bond length of isolated O_2 are 2.26 Å, 3.56 Å, and 1.24 Å, respectively, in good agreement with the experimental values of 2.285 Å, 3.585 Å,[25] and 1.21 Å.[26] The O_2 is placed on one side of the slab, namely, on the top surface, whereas the bottom two layers are fixed. All other Be layers as well as the oxygen atoms are free to move during the MD simulations.

We start our simulations with different orientations of an O_2 molecule placed over different surface sites [one representative case is illustrated in Fig. 1(a)]. In all initial configurations, the mass center of the O_2 molecule is initially set to be 4 Å away from the metal surface. In the cases of Al(111) and Mg(0001), the failure of adiabatic FPMD simulations in

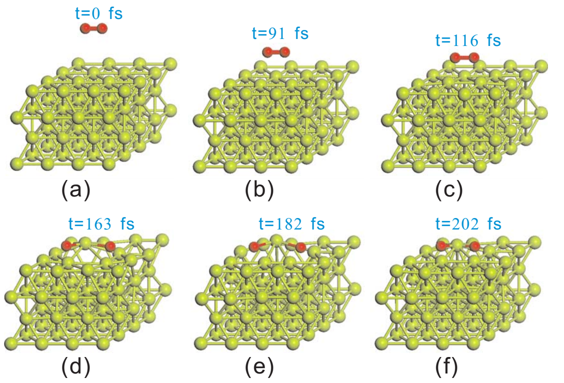

FIG. 1. (Color online) Snapshots from a FPMD simulation of the dissociative chemisorption of an O_2 molecule on the Be(0001) surface. Only the four outermost Be layers are shown. Red and yellow balls, respectively, represent oxygen and Be atoms. (a) Initial geometry (simulation time $t=0$ fs) with the molecule parallel to the surface. The distance between the center of mass of the molecule and the topmost surface layer is 4.00 Å. [(b)–(e)] The atomic geometry of the adsorption system at $t=91$, 116, 163, and 182 fs. (f) Final configuration in equilibrium after relaxation ($t=202$ fs). The final O-O distance is 2.33 Å.

producing an activated-type dissociation process has been ascribed to the unphysical output that charge transfer occurs at any molecule-metal distance, which has led to speculations that nonadiabatic effects may play an important role in the oxygen dissociation process at these metal surfaces with simple *sp* electrons.[19,27–31] However, this requirement is not always needed. In our calculations, we find that at enough molecule-metal distance (≥4.0 Å), the unphysical large-distance charge-transfer effect does not happen between O_2 and the Be(0001) surface. The calculated spin-split electronic states of O_2 in close to the Be(0001) surface shows no change with respect to the free molecule. The lowest unoccupied molecular orbital remains empty and the charge-density difference is zero everywhere. Subsequently, the molecular bond length and spin of O_2 are not influenced at all by the presence of the Be(0001) surface.

For the adsorption of the first O_2 molecule, the substrate atoms are initially at rest. Since we have known from our static calculations that an energy barrier is needed for the dissociation of O_2 molecule on the clean Be(0001) surface,[19] we set two different initial kinetic energies for the O_2 molecule, respectively, 0.06 and 0.6 eV. From the MD simulations, we find that the O_2 molecule with the initial kinetic energy of 0.06 eV does not dissociate at all on the Be(0001) surface after 3 ps but the one with the initial kinetic energy of 0.6 eV easily dissociate in 200 fs. These results clearly prove the existence of an energy barrier during the O_2 dissociation on the Be(0001) surface, whose value is between 0.06 and 0.6 eV. The structural evolution for the O_2 dissociation with the initial kinetic energy of 0.6 eV is depicted in Fig. 1. We can see that the surface Be atoms have no motions until $t=116$ fs. From the time $t=116$ to 163 fs, one surface Be atom is pulled out a little during the dissociation of the two oxygen atoms. After $t=116$ fs, the two oxygen atoms steadily adsorb at the two hcp hollow sites and the adsorption system begins to vibrate in its intrinsic frequencies.

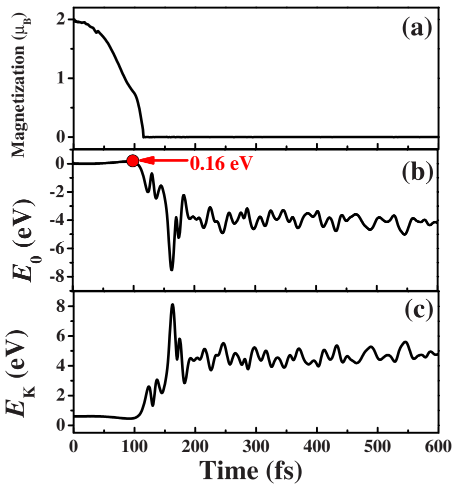

FIG. 2. (Color online) (a) The spin magnetization of the system in a FPMD simulation of the dissociative chemisorption of an O_2 molecule on the Be(0001) surface. [(b) and (c)] The electronic free energy and kinetic energy of the system in the same FPMD simulation. The electronic free energy of an O_2 molecule plus that of the clean Be(0001) surface is set to zero in (b).

The spin and electronic free energy of the adsorption system during the dissociation process of Fig. 1 are shown in Fig. 2. We can see from Fig. 2(a) that the total spin of the system gradually decrease into zero as the O_2 molecule gets closer to the Be surface and dissociates. For the electronic free energy of the adsorption system, we set the value before adsorption happens (i.e., the electronic free energy of an O_2 molecule plus that of the clean Be(0001) surface) to be zero. When the O_2 molecule gets to be 2.36 Å from the Be surface, the electronic free energy is enlarged by 0.16 eV as shown in Fig. 2(b), which corresponds to the energy barrier for the O_2 dissociation on the clean Be surface. The value difference with our static potential energy surface result[19] comes from that we have chosen a much larger 4×4 supercell and the motions of surface Be atoms are considered here. Accompanying with the enlargement of the electronic free energy, the kinetic energy decreases by 0.16 eV, as shown in Fig. 2(c). After that, the kinetic energy begins to fluctuate, and reach the equilibrium value of 4.52 eV at $t=202$ fs. At the same time, the electronic free energy of the adsorption system becomes −3.92 eV.

Although the adsorption energy is large, we see no movement of the dissociated oxygen atoms during the FPMD simulation. Instead, the oxygen atoms steadily adsorb at two neighboring hcp hollow sites and vibrate. Comparing with the hot oxygen atoms on the Al(111) surface, which move away very fast after dissociation,[9] the dissociated oxygen atoms on the Be(0001) surface are not so hot, without any fast movements. Thus, our finding for the dissociation mechanism of O_2 is different from the hot-atom picture, which was theoretically understood mostly through simulating the $O_2/Al(111)$ prototype.[9] The different dissociation mechanisms may come from different surface electronic structures of Al and Be. In particular, our result that the dissociated oxygen atoms have low mobility is very consistent with the experimental observations that the surface oxi-

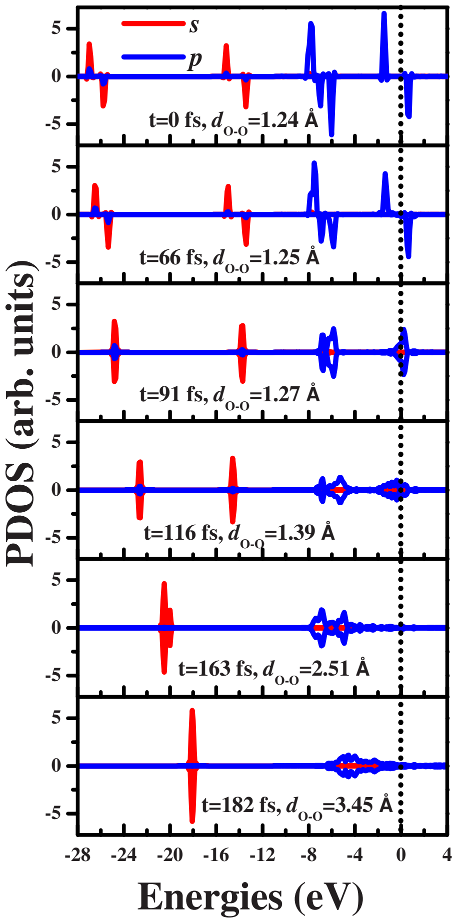

FIG. 3. (Color online) Spin-resolved densities of states around the two oxygen atoms at different times, in a FPMD simulation of the dissociative chemisorption of an O_2 molecule on the Be(0001) surface. The *s* and *p* electronic states are shown, respectively, in red and blue lines.

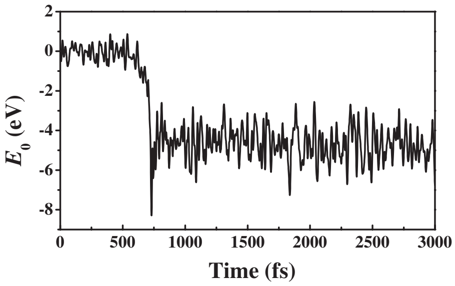

FIG. 4. The electronic free energy of the adsorption system in the FPMD simulation for the dissociative adsorption of the second O_2 molecule. The electronic free energy of the oxygen-adsorbed Be surface plus that of the second O_2 molecule is set to zero.

dation of Be begins by forming separate nucleation islands.

The evolution of the spin configurations during the adsorption and dissociation of O_2 molecules on metal surfaces is of great theoretical importance.[19,28] Since the adiabatic calculations are suitable enough for the O_2/Be(0001) system, we would like to take a look at the evolutions in spin configurations of O_2 during the dissociative adsorption process. Figure 3 shows the spin-resolved densities of states for the two oxygen atoms at different times. We can see that at the very beginning, the O_2 molecule is in the spin-triplet ground state with the spin splittings of about 2 eV for both bonding and antibonding orbitals. Until $t=66$ fs, no big changes happen in the electronic structures of O_2, except that the spin splitting decreases about 0.2 eV for all orbitals. After that, the total spin starts to distribute both around oxygen and neighboring Be atoms. Then at the transition state ($t=91$ fs), the spin splitting decreases to be negligible around each oxygen atom. We can see that the spin quenching effect from electronic hybridizations between O_2 and the Be(0001) surface happens really fast. After crossing the transition state, the electronic free energy quickly goes down since the two oxygen atoms are separated and begin to bond with surface Be atoms. At the meantime, the energy difference between bonding and antibonding orbitals of O_2 reduces and finally to be zero at $t=182$ fs. In total, there are two stages during the O_2 dissociation. At the first stage (i.e., before the transition state), the electronic interaction results in spin quenching and makes the two oxygen atoms to separate from each other. At the second stage, the two oxygen atoms begin to bond with Be atoms, blurring the distinction in bonding and antibonding orbitals.

It has been experimentally reported that the surface oxidation of Be begins by forming separate oxide islands. Since it has been revealed that the dissociated oxygen atoms have low mobilities on the Be(0001) surface, the formation of separate oxide islands has no connection with oxygen diffusion. We then perform a consecutive FPMD simulation for the adsorption of a new O_2 molecule on the Be(0001) surface, starting with the new O_2 molecule placed 4 Å from the relaxed surface obtained in the previous simulation. During this FPMD simulation, the substrate oxygen and Be atoms are no longer at rest with their initial velocities taken from the equilibrium state of the previous simulation. During this consecutive FPMD simulation, it is found that the new O_2 molecule can dissociate even with zero initial kinetic energy. At the beginning of the process, the temperature within the 4×4 surface area increases by about 700 K because of the dissociative adsorption of the previous O_2 molecule. When the second O_2 molecule is introduced, it is instantaneously activated from the spin-triplet ground state to the spin-singlet excited state under such a high temperature. From our FPMD simulation, we see that the second O_2 molecule dissociates easily in 600 fs from its spin-singlet state. The electronic free energy of the system during the consecutive FPMD simulation is shown in Fig. 4, from which one can see that the dissociation of the second O_2 molecule further causes a decrease of 4.76 eV in electronic free energy. And the temperature of the system is thus further elevated by 700 K. Based on these FPMD simulation results, we propose an atomistic model for the surface oxidation of Be. In our model, the dissociation of the first introduced O_2 molecules needs to overcome an energy barrier, which is responsible for the low sticking coefficient of oxygen at very low temperatures. However, the subsequently adsorbed O_2 molecules will barrierlessly dissociate around the adsorption areas, resulting in the formation of separate oxide islands at higher temperatures.

In summary, we have systematically investigated the adsorption and dissociation of O_2 molecules on the Be(0001) surface within spin-polarized first-principles molecular-dynamics simulations. We find that the previous hot-atom atomistic model is not suitable for the oxygen dissociation and oxide nucleation on the Be(0001) surface. The O_2 dissociation is found to be an activated process on the Be(0001) surface and the dissociated oxygen atoms are not very mobile. Based on our calculational results, we propose an atomistic model for the surface oxidation of Be, in which the dissociation of the first introduced O_2 molecules needs to overcome an energy barrier while the subsequent O_2 molecules dissociate barrierlessly at the same surface area. In this way, separate oxide islands form on the metal surface and grow up together in a lateral way as more oxygen molecules are introduced.

This work was supported by the NSFC under Grants No. 10904004 and No. 60776063.

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