"Hot-Atom" O_2 Dissociation and Oxide Nucleation on Al(111)

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We propose an atomistic model for the nucleation of aluminum oxide on the Al(111) surface derived from first principles molecular dynamics simulations. The process begins with the dissociative adsorption of O_2 molecules on the metal surface, which occurs via a "hot-atom" mechanism driven by the partial filling of the σ^* antibonding molecular orbital of O_2. During the subsequent hyperthermal motion, O atoms can be spontaneously incorporated underneath the topmost Al surface layer, initiating the nucleation of the oxide far below the saturation coverage of one (1×1) O adlayer.

Metal surfaces in contact with the atmosphere, with gold being the only exception, are thermodynamically allowed to react with oxygen molecules to form a metal oxide [1]. Depending on its chemical reactivity, the metal can oxidize completely, as in the case of iron, or can be passivated by a thin layer of amorphous oxide, as in the case of chromium and aluminum. This oxide layer governs the interactions of the metallic material with the external environment, and is responsible, for instance, for the catalytic activity of the metal particles in automobile catalysts [2] or for the bioactivity of metallic implant surfaces in the human body [3]. Therefore, the formation of superficial oxide phases on metals is a problem of deep scientific importance and of wide technological relevance. Nevertheless, detailed atomistic models for the nucleation of superficial metal oxides are not presently available. In particular, no spin-unrestricted first principles molecular dynamics (FPMD) studies of the chemisorption of O_2 molecules on metal surfaces or of their initial oxidation have been performed to date.

In this Letter, we study the nucleation of aluminum oxide after the adsorption of O_2 molecules on the Al(111) surface by means of totally unconstrained FPMD techniques [4] based on the Car-Parrinello scheme [6], using recently developed algorithms which are particularly suited to the study of metallic systems [7,8]. Because of its relative chemical simplicity, aluminum is considered an ideal model system to study the initial stages of metal oxide formation by means of both experimental [9–14] and theoretical [5,15–18] techniques. The chemisorption of oxygen on the bare Al(111) surface occurs either via a dissociative or via an abstractive channel. The dissociative channel leads to the chemisorption of both atoms separated by distances as large as 3 times the metal-metal distance [13], which is indicative of a "hot-atom" dissociation mechanism [19]. The abstractive channel leads to chemisorption of only one atom, while the second atom is ejected into the gas phase [11,12]. While the abstractive channel dominates at extremely low oxygen coverages and at low translational kinetic energies of the impinging oxygen molecules, at increasingly high translational energies (above ~ 0.3 eV) and oxygen coverages, "normal" dissociative chemisorption occurs with increasing probability [11,16].

Measurements of the sticking coefficient of O_2 on Al(111) as a function of the translational kinetic energy of the molecules show that chemisorption is an activated process [14]. On the other hand, state-of-art quantum mechanical calculations based on density-functional theory (DFT) were not able to find any barrier associated with the chemisorption process [5,15]. In Ref. [5], the abstractive channel was found to be activated but thermodynamically allowed when dioxygen molecules hit the surface in an end-on orientation [20]. However, a drawback of all static calculations is that the possibility of spontaneous changes of the orientation of the impinging molecule in order to find the energetically most favorable path along the potential energy surface (steering effects) is not fully taken into account. On the other hand, steering effects, together with the gain in kinetic energy during the adsorption process, can open reaction channels which appear to be forbidden in static calculations [21]. Performing unconstrained dynamical simulations thus appears to be essential for a more comprehensive understanding of the chemisorption processes.

We perform a total of six FPMD simulations, starting with different orientations of an O_2 molecule placed over different surface sites (two representative cases are illustrated in Figs. 1 and 2). In all cases, the molecule is initially at rest. The observed chemisorption paths are characterized by a number of common features which are independent of the initial conditions. These are summarized below. When the center of mass of the molecule is about 3.5 Å above the surface, the integrated total spin density $\Delta\rho$ is about 1.8 electrons, indicating a partial donation of electronic charge into the π^* orbitals of O_2, whose ground state is a triplet with two unpaired electrons [Fig. 1(a)]. Consistent with this, the Fermi level of the system is found to be aligned with the lower edge of the lowest unoccupied molecular orbital (LUMO) peak of the local density of states projected onto the O atoms [Fig. 2(a)]. After starting the dynamics, the molecule is
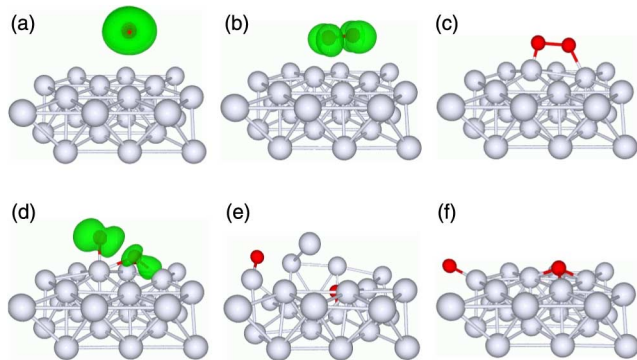
FIG. 1 (color online). Snapshots from a FPMD simulation of the dissociative chemisorption of an O_2 molecule on the Al(111) surface. Only the two outermost Al layers are shown. The spin density of the system is depicted as a semitransparent isosurface. (a) Initial geometry (simulation time $t = 0$) with the molecule parallel to the surface and perpendicular to an Al-Al bridge. The distance between the center of mass of the molecule and the topmost surface layer is 3.53 Å. (b) $t = 283$ fs. (c) Molecular adsorption with quenching of the spin density ($t = 312$ fs). (d) Partial asymmetric filling of the σ^* molecular orbital and dissociation of the O-O bond ($t = 348$ fs). (e) After the dissociation, one of the atoms spontaneously penetrates through the topmost Al layer ($t = 493$ fs). (f) Final configuration, after relaxation ($t = 1$ ps). The final O-O distance is 5.90 Å.

spontaneously attracted toward the surface, and the corrugated potential energy surface steers the molecule in the direction of the most favorable adsorption site so that a barrierless chemisorption channel is found in all the
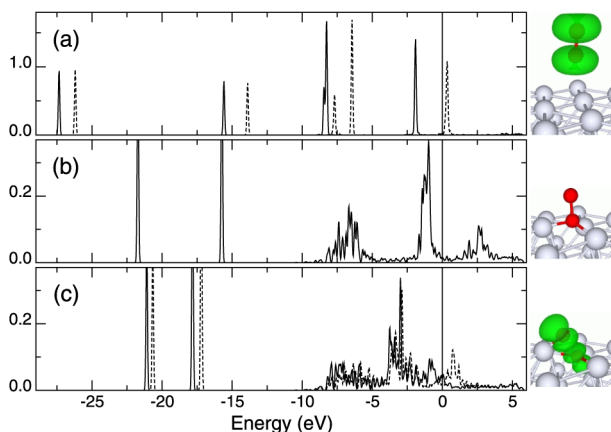

FIG. 2 (color online). Evolution of the local density of states projected onto the O atoms during the adsorption of O_2 on Al(111) (left) and correspondent snapshots from a FPMD simulation started with the molecule perpendicular to the surface over a fcc hollow site (right). The spin density of the system is depicted as a semitransparent isosurface. In the graphs the continuous and the dotted lines correspond to the majority and minority spin manifolds, respectively. The vertical line indicates the Fermi level. (a) Initial configuration (simulated time $t = 0$). (b) Adsorption ($t = 464$ fs). (c) Dissociation ($t = 493$ fs).

cases investigated. In particular, spontaneous chemisorption also occurs starting with the molecule parallel to the surface and perpendicular to a bridge site (Fig. 1), which is the only channel where an activation barrier for the adsorption was found in the static calculations of Ref. [5]. The adsorption process is characterized by increasing donation of electrons from the surface into the π^* antibonding orbitals of the molecule [Figs. 1(a)–1(c)], which corresponds to a gradual sinking of the LUMO peak below the Fermi level, until the spin of the system is fully quenched to zero [Fig. 2(b)]. When both O atoms bind to the surface and the O-O distance becomes larger than ~1.8 Å, the σ^* antibonding molecular orbital reaches the Fermi edge and becomes partially occupied. Interestingly, filling of this orbital occurs in an asymmetric manner and is directly visible by imaging the spin density of the system [Figs. 1(d) and 2(c)]. The O-O bond dissociates as a consequence of this process, the O-O distance increasing abruptly in a way that is indicative of a non-thermal, hot-atom mechanism. Namely, in the simulation shown in Fig. 1, the O-O distance increases from 1.85 to 3.85 Å in 58 fs of simulated time, which corresponds to an initial mean velocity of 1.72×10^3 m/s per atom. It should be noted that, while there is donation of electrons into the antibonding orbitals of O_2, the bonding orbitals "melt" in the sea of delocalized electrons below the Fermi level (see Fig. 2), so that the charge on the adsorbed molecule is always well below two electrons, as pointed out in Ref. [15]. The hyperthermal dissociation is therefore not triggered by Coulomb repulsion between the charged O atoms, but by the Pauli repulsion between the partially occupied p-type orbitals along the O-O axis [Figs. 1(d) and 2(c)]. The kinetic energy associated with the motion of the hot atoms after the dissociation is high enough to push one of the O atoms below the topmost Al layer while one Al atom is pulled out of the surface [Fig. 1(e)]. However, in the subsequent dynamics, the O atom emerges again above the surface and is soon stably adsorbed in a hollow surface site. The final O-O distances after relaxation range from 2.9 to 5.9 Å in the different simulations, i.e., between one and two Al-Al distances [22].

Notably, in all the cases considered, we observe dissociation only when *both* O atoms are bound to the surface, and in none of the simulations we do see an abstractive adsorption process. Furthermore, in contrast with experiments [14], but in agreement with existing DFT calculations on Al [5,15] and on noble metals such as silver [24] and platinum [25], we found no energy barrier for the molecular adsorption in all the simulations performed. The lack of a barrier might be related to the fact that in the generalized gradient approximation (GGA)-DFT calculations there is no gap between occupied and unoccupied electronic states; i.e., the LUMO 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 orbitals, which finally drives the adsorption. A barrier would be found if the repulsion between the filled orbitals and the surface states occurred prior to orbital hybridization. In this case, chemisorption is likely to occur as the result of nonadiabatic effects, and indeed a nonadiabatic electron transfer model is able to explain qualitatively the measured low sticking coefficient of O_2 at low translational energies [18]. We must conclude that the harpooning of electrons at a distance from the surface is also responsible for the occurrence of the abstractive adsorption channel, which is never observed in our adiabatic simulations. The abstraction of atoms can be either due to dissociation in midair after electron transfer or to adsorption of O_2^- or O_2^{2-} molecules, which cannot be simulated within our formalism. Instead, oxygen chemisorption is expected to take place via an adiabatic dissociative channel on the Pt(111) surface, where abstractive adsorption is never observed and the hot-atom dissociation is activated by phonons [19].

On Al(111), at higher oxygen coverages (~ 0.1 ML), the adsorbed atoms start forming (1×1) islands, and the adsorption of molecules at the island boundaries is thought to occur predominantly via the normal dissociative chemisorption channel [16]. At coverages of ~ 0.2 ML, oxide nuclei start to form at the boundaries between adatom islands and the bare metal surface via a nonthermal mechanism, which is most probably driven by the motion of hot atoms [10]. Therefore, the event accessible to our simulation (the normal dissociative chemisorption) is common under the conditions where superficial oxide phases start forming. As a consequence, adiabatic FPMD simulations can be legitimately used to investigate the issue of oxide nucleation.

To this aim, we perform a series of consecutive FPMD simulations of the adsorption of oxygen molecules on the Al(111) surface, each time starting with a new O_2 molecule placed near the relaxed surface obtained in the previous simulation. After the dissociative chemisorption of the first O_2 molecule, a second molecule dissociates in the same way, and, at the end of the simulation, four O atoms are stably adsorbed in hollow surface sites. When a third molecule approaches this system [Fig. 3(a)], after dissociation [Fig. 3(b)] one Al atom is pulled out of the topmost surface layer [Fig. 3(c)], while one of the previously adsorbed O atoms falls into the vacancy created and remains stably incorporated underneath the topmost surface layer [Fig. 3(d)]. This process is indicative of the nucleation of an oxide phase, as pointed out in Ref. [10]. The final oxygen coverage in this simulation is 0.5 ML, that is, well below the saturation coverage of one (1×1) O adlayer. In the experiments, in fact, the nucleation of oxide is found to start at even lower coverages (~ 0.2 ML). The simulations of oxygen adsorption are continued until a coverage of 1 ML is reached. The final structure is shown in Fig. 4, where the initial formation of an amorphous oxide layer is clearly visible.
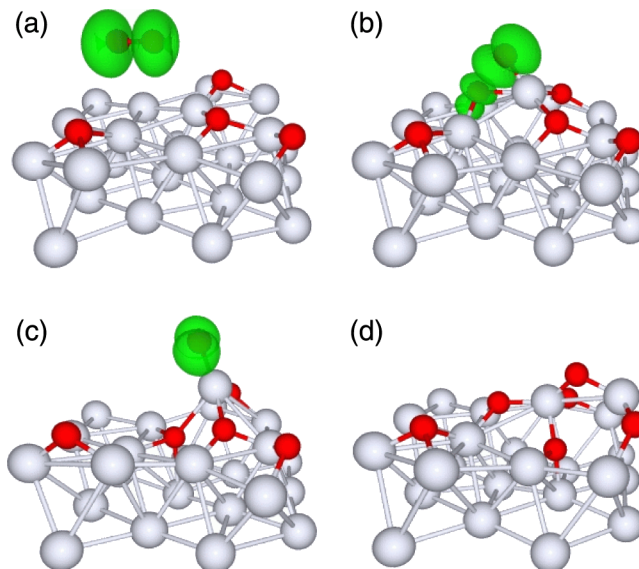

FIG. 3 (color online). Snapshots from a FPMD simulation showing the nucleation of aluminum oxide on the Al(111) surface after adsorption of three O_2 molecules. Only the two outermost Al layers are shown. The spin density of the system is depicted as a semitransparent isosurface. (a) Initial configuration (simulated time $t = 0$). (b) Dissociation of the O-O bond ($t = 145$ fs). (c) $t = 247$ fs. (d) Final structure ($t = 1$ ps). The oxygen coverage is 0.5 ML.

Notably, our simulations are performed starting from relaxed surfaces and immobile molecules, i.e., virtually at 0 K. Nevertheless, after the dissociation, hot oxygen atoms are inevitably created, which can *spontaneously* penetrate through the topmost Al surface layer. At a coverage of 0.5 ML, this event initiates the nucleation of an oxide phase in a process which does not involve long-range mass transport but only local atomic rearrangements, which is consistent with previous STM experiments [10]. From these results, the possibility of creating a saturated (1×1) oxygen adlayer starting from cold surfaces seems to be excluded. This finding has important consequences in view of possible simulations on larger scale, e.g., with Monte Carlo techniques, where it has been assumed so far that the events of adsorption
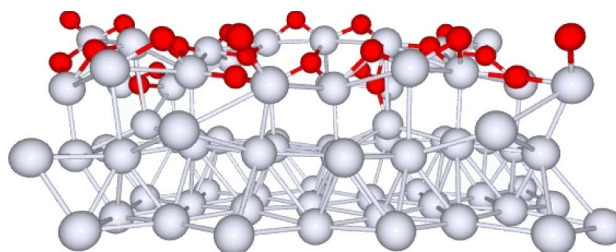

FIG. 4 (color online). Structure of the Al(111) surface after the adsorption of six oxygen molecules in six consecutive FPMD simulations. Only the three outermost Al layers are shown, and the simulation cell is repeated twice in the longitudinal direction. The oxygen coverage is 1 ML.

and oxide formation can be separated in time [17]. On the contrary, we find that these events take place *simultaneously* on the picosecond time scale, the oxide nucleation being a direct consequence of the hot-atom dissociative adsorption.

In conclusion, the dissociative chemisorption of O_2 on Al(111) in the adiabatic limit is triggered by partial filling of the σ^* antibonding molecular orbital of dioxygen due to hybridization with the surface states [26]. During the subsequent hyperthermal motion, the O atoms can be spontaneously incorporated underneath the topmost Al surface layer, initiating the nucleation of oxide phases at an oxygen coverage which is well below the saturation coverage of one (1×1) O adlayer, in full agreement with the existing experimental results.

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