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Ab initio molecular dynamics study of ion-surface interactions

Johanna Rosén[a,*], Jochen M. Schneider[a], Karin Larsson[b]

[a]*Materials Chemistry, RWTH-Aachen, Kopernikusstr. 16, D-52056 Aachen, Germany*
[b]*Department of Materials Chemistry, The Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden*

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Abstract

Ion-surface collisions have been investigated theoretically using ab initio molecular dynamics within density functional theory. The temporal evolution of the position of the bombarding ion, as well as its nearest neighbors, was studied for initial kinetic energies of 0 and 3.5 eV (0 and 5 km/s, respectively). Also investigated was the ion-surface interaction prior to collision and the following energy transfer, as indicated by changes in ion velocity. At 3.5 eV collision energy, the calculation results suggest the formation of local structural disorder within the simulation time frame studied. These results are of fundamental importance for an increased understanding of the ion-surface interaction during a collision event, with resulting changes in atomic level structure.

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Keywords: A. Surfaces; D. Structural disorder

1. Introduction

Alumina, α-Al_2O_3, is of considerable importance due to diverse applications ranging from corrosion and wear protection in mechanical systems to dielectric media in microelectronics. Low temperature vapor phase condensation ($\leq 250\,^{\circ}C$) of alumina is known to result in an amorphous structure [1], and understanding the influence of growth parameters (e.g. ion energy) on the atomistic mechanisms that are active during the growth process, is essential for controlling microstructure evolution.

Classical Molecular dynamics (MD) simulations based on empirical potentials have proven to be useful for studying ion-surface interactions. Several material systems have been investigated for this purpose, see for example Refs. [2–7]. The questions addressed have been directed towards the influence of impinging ion energy on adatom diffusion/bulk damage [2], final adatom position [3], film morphology [4], film structure/density [5], surface exchange diffusion [6], and stress generation [7]. Generally, it was shown that the ion energy is important for these properties/processes.

Ab initio MD may be an alternative to classical MD, where instead of empirical potentials the electronic structure is explicitly treated, and therefore many-body forces, electronic polarization, bond-breaking and forming events can be described. To our knowledge, no ab initio MD simulations of ion-surface collisions have previously been reported in the literature. Here, the results of first principles simulations within density functional theory (DFT) are presented, investigating collisions between an Al^+ ion and an α-Al_2O_3 surface, where the effect of ion movement on the ion-surface energy transfer mechanism and the geometrical structure is investigated. These results may be of importance for understanding microstructure evolution.

* Corresponding author. Tel.: +49 241 8025988; fax: +49 241 8022295.
E-mail address: rosen@mch.rwth-aachen.de (J. Rosén).

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2. Method

The interaction between an Al^+ ion moving towards an O-terminated α-Al_2O_3 (0001) surface is investigated. The collision site is marked with X in Fig. 1(a). The termination is motivated by (a) the presence of oxygen during film growth and (b) the detection of hydrogen in the plasma [8], where the latter has been shown to stabilize the O termination [9]. Al^+ was investigated because it is the most abundant ion in an Al arc plasma at elevated oxygen pressures [8].

The surface was modelled in a super-cell approach, consisting of nine atomic layers (60 atoms) where the two bottom layers were fixed to simulate bulk conditions. Different collision sites, as well as different collision energies, were tested, in order to find conditions where the cell depth was large enough and where collision effects from adjacent cells could be neglected. Hence, an upper limit of 3.5 eV was identified for collisions where Al^+ was positioned directly above a surface atom. Furthermore, the reproducibility within the present investigation was tested, which resulted in no observable variations (the same final geometry of the system). For more information regarding test calculations preceding the final and optimised super-cell size, see Ref. [10]. Ab initio MD was carried based on the microcanonical ensemble, using periodic boundary conditions within the framework of density functional theory (DFT). The program package CASTEP from Accelrys Inc. was used for this purpose [11]. The electronic orbitals were represented by a plane-wave expansion up to a cutoff energy of 300 eV, with four *k*-points generated according to Monkhorst–Pack [12]. Electron–ion interaction was described by an ultrasoft pseudopotential in the Kleinman–Bylander form [13], and local density approximation (LDA) was used for exchange and correlation interactions between the electrons. The temperature of the system was set to 330 K, and the simulations were performed in time steps of 1 fs. The total simulation time (0.3 ps) chosen corresponds to when the individual atoms oscillate around a momentarily stable average distance from their equilibrium bulk positions, as exemplified in Fig. 1(b) (for an ion-surface collision at 3.5 eV).

The temporal evolution of the position of the bombarding ion, as well as its nearest neighbors, has been investigated for initial kinetic energies of 0 and 3.5 eV (0 and 5 km/s, respectively). Also studied is the ion-surface interaction prior to collision and the following energy transfer, through changes in ion velocity.

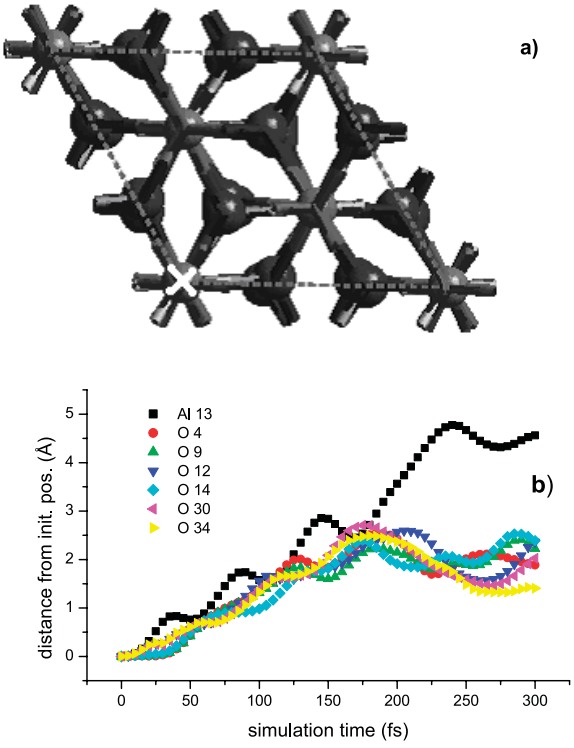

Fig. 1. (a) Top view of a part (1/4) of the α-Al_2O_3 (0001) surface, showing the ion-surface collision site investigated (marked with an X). (b) (Color online) Distance from initial equilibrium bulk position vs. simulation time for the atoms closest to (and below) the collision site (3.5 eV collision energy).

3. Results and discussion

The effect of ion energy on the local temporal structure evolution is presented in Figs. 2 and 3, showing atom/ion coordinates in time steps of 5 fs in a collision between an Al^+ ion (denoted Al_c) and an oxygen terminated α-Al_2O_3 (0001) surface. Only nearest neighbors to the collision site are shown here. Fig. 2 presents the result of no initial velocity of Al_c. The inserted square is a top view of the surface segment investigated, where the symbols indicate the initial relative position of Al_c and its neighbors. The main graph shows the change in position for the atoms, in (a) *yz*-plane and (b) *xz*-plane, during a simulation time of 0.27 ps. To begin with, Al_c is accelerated towards the surface without deviating significantly in *x*- or *y*-direction, indicating a local potential energy minimum at the underlying surface site. When reaching the surface, Al_c does not penetrate the topmost layer, but diffuses within approximately a 1 Å radius in the *xy*-direction. In addition to temperature oscillations (calculated to <1 fm in amplitude [14]), the surrounding ions move subsequent to adsorption; on average approximately 1 Å from the initial position.

As the initial kinetic energy is increased to 3.5 eV (5 km/s), Al_c penetrates the surface (Fig. 3). Larger displacements are observed (as compared to 0 eV energy, in Fig. 2), for all ions, in both *xz*- and *yz*-plane, most pronounced in *z* direction. The largest changes in nearest neighbors distance are between the atom at the collision site (in the second layer) and the topmost surface atoms, with increments above 100%. (For the 0 eV case, the