

*Ab initio* molecular dynamics study of hydrogen removal by ion–surface interactions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 L137

(<http://iopscience.iop.org/0953-8984/17/15/L01>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 20:37

Please note that [terms and conditions apply](#).

## LETTER TO THE EDITOR

***Ab initio* molecular dynamics study of hydrogen removal by ion–surface interactions**Johanna Rosén<sup>1</sup>, Karin Larsson<sup>2</sup> and Jochen M Schneider<sup>1</sup><sup>1</sup> Materials Chemistry, RWTH-Aachen, D-52056 Aachen, Germany<sup>2</sup> Department of Materials Chemistry, Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden

Received 20 December 2004, in final form 15 February 2005

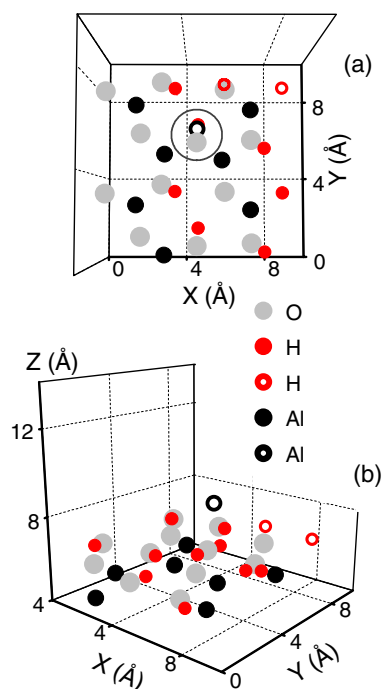
Published 1 April 2005

Online at [stacks.iop.org/JPhysCM/17/L137](http://stacks.iop.org/JPhysCM/17/L137)**Abstract**

The energy dependence of surface reactions has been investigated through *ab initio* MD simulations for collisions between Al<sup>1+</sup> and a gibbsite surface. No change in surface composition was observed for 0 eV initial kinetic energy of Al<sup>1+</sup>. An increase in energy to 3.5 eV resulted in extended surface migration of hydrogen, subsequent H<sub>2</sub> formation and desorption from the surface. These results may be understood based on thermodynamics and an increase in entropy upon H<sub>2</sub> formation. They are of fundamental importance for an increased understanding of thin film growth through the correlation between ion energy and film composition. They may also indicate a pathway to affect impurity incorporation during film growth.

(Some figures in this article are in colour only in the electronic version)

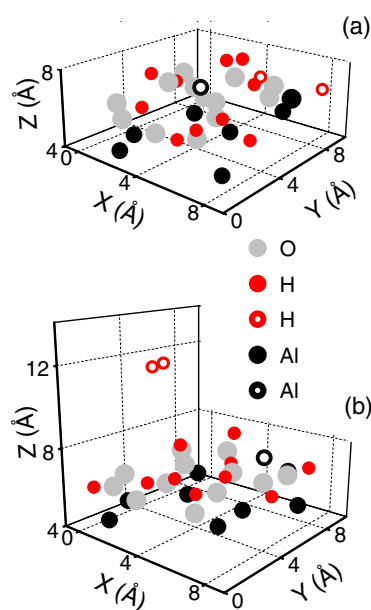
Alumina exhibits advantageous properties suitable for applications in wear and corrosion protection [1, 2] and as diffusion barriers [3]. Thin films can be produced by a wide spectrum of vacuum based vapour deposition techniques, which all are characterized by the presence of residual gas. In high vacuum growth systems H<sub>2</sub>O is the most abundant residual gas [4], and a source of hydrogen. Previous studies have shown hydrogen incorporation in alumina thin films [5]. Furthermore, it is well known that bulk alumina forms hydroxides [6]. The unintentional incorporation of hydrogen affects the composition and microstructure [7, 8], and hence the material properties [7]. It is therefore desirable to enable growth excluding this incorporation. The amount of hydrogen in strontium titanate films was shown to be strongly affected by substrate temperature [8]. In addition to substrate heating, energy can also be supplied to the growing film through ion bombardment. This was exemplified in a Monte Carlo study [9] on oxygen desorption induced by incident ions on a Ti surface. However, the effect of ion energy on hydrogen incorporation has to our knowledge never previously been investigated. Here, an ion–surface collision event is simulated, investigating the energy dependence of surface reactions including hydrogen.



**Figure 1.** (a) Topview of the topmost surface segment with marked collision site. (The different colours represent the different atomic species, and the hollow symbols are introduced to discern the bombarding Al ion and two of the surface hydrogen atoms.) (b) Sideview of the same surface segment.

*Ab initio* molecular dynamics (MD) is an alternative to the widely used classical MD, where instead of empirical potentials the electronic structure is explicitly treated. This enables the description of many-body forces, electronic polarization and bond-breaking and forming events. *Ab initio* MD simulations of ion–surface collisions has previously shown a strong energy dependence of the formed local structural disorder [10]. In this letter, the corresponding first principles MD simulations within density functional theory (DFT) are presented, investigating collisions between an  $\text{Al}^{1+}$  ion and a gibbsite,  $\text{Al}(\text{OH})_3$ , surface. The effect of ion energy on the hydrogen configuration was studied, and we present evidence for collision induced  $\text{H}_2$  removal. This may be understood by considering thermodynamic principles. The results are of fundamental importance for an increased understanding of ion energy versus film composition.

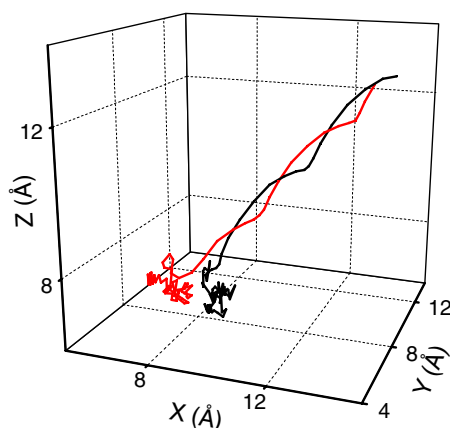
The hydrogen terminated (001) surface was chosen for the study, which is the experimentally observed preferential cleavage surface [11]. An  $\text{Al}^{1+}$  ion (the most abundant ion in an arc plasma at elevated pressures [12, 13]) was initially positioned  $2.2 \text{ \AA}$  above a horizontal O–H bond; see the topview of the topmost surface segment with marked collision site in figure 1(a). (The particles marked with hollow symbols are the bombarding  $\text{Al}^{1+}$  and two hydrogen atoms further discussed below.) The surface was modelled in a supercell approach, consisting of 10 atomic layers (112 atoms), where the five bottom layers were fixed to simulate bulk conditions. Test calculations prior to previous studies of ion–surface interaction [10, 14] were assumed to be valid also for the present investigation, considering a larger cell size and an increased number of atoms in the cell for this study. The *ab initio*



**Figure 2.** (a) The configuration after 0.375 ps, for 0 eV initial energy of the bombarding ion. (b) The configuration after 0.375 ps, for 3.5 eV initial energy of the bombarding ion.

MD simulation was carried out in the microcanonical ensemble within the framework of DFT, using the program package from Accelrys Inc. [15]. The choice of ensemble is justified by the thin film growth related condition of a constant number of particles  $N$ , constant volume  $V$  and conserved energy  $E$  during an ion–surface collision. The nuclear motions were treated by solving the Newtonian equations using the velocity Verlet propagator [16]. The electronic orbitals were represented by a plane wave expansion up to a cutoff energy of 260 eV, with 1  $k$ -point (generally sufficient for nonmetallic systems [17]) generated according to Monkhorst–Pack [18]. Local density approximation (LDA) was used for exchange interaction between the electrons, and electron–ion interaction was described by an ultrasoft pseudopotential in the Kleinman–Bylander form [19]. Furthermore, the initial temperature of the system was set to 330 K.

A sideview of the initial geometry of the topmost surface layers is shown in figure 1(b). The  $\text{Al}^{1+}$  ion was assigned an initial kinetic energy (in the vertical direction) of 0 and 3.5 eV, and in subsequent simulations the temporal evolution of the ion/atom positions were studied in time steps of 1 fs. With an initial energy of 0 eV, the  $\text{Al}^{1+}$  ion was attracted towards the surface, and incorporated in the surface layer; see figure 2(a), corresponding to the configuration after 0.375 ps. In contrast, the 3.5 eV ion–surface bombardment changed the surface composition; see figure 2(b). The  $\text{Al}^{1+}$  ion approached the surface, stayed in the top surface layers, and caused (after  $\sim 0.3$  ps)  $\text{H}_2$  desorption from the surface. The corresponding simulation trajectories of the molecule forming hydrogen are shown in figure 3, with final coordinates equal to those shown in figure 2(b) using periodical boundary conditions. Both simulations were continued for 0.5 ps, but no further changes in surface composition were observed. When comparing the final surface configurations, more outward relaxation is observed for the unchanged surface composition, consistent with previously reported findings of  $H$  dependent relaxation of hydrogen terminated  $\alpha\text{-Al}_2\text{O}_3$  surfaces [20].

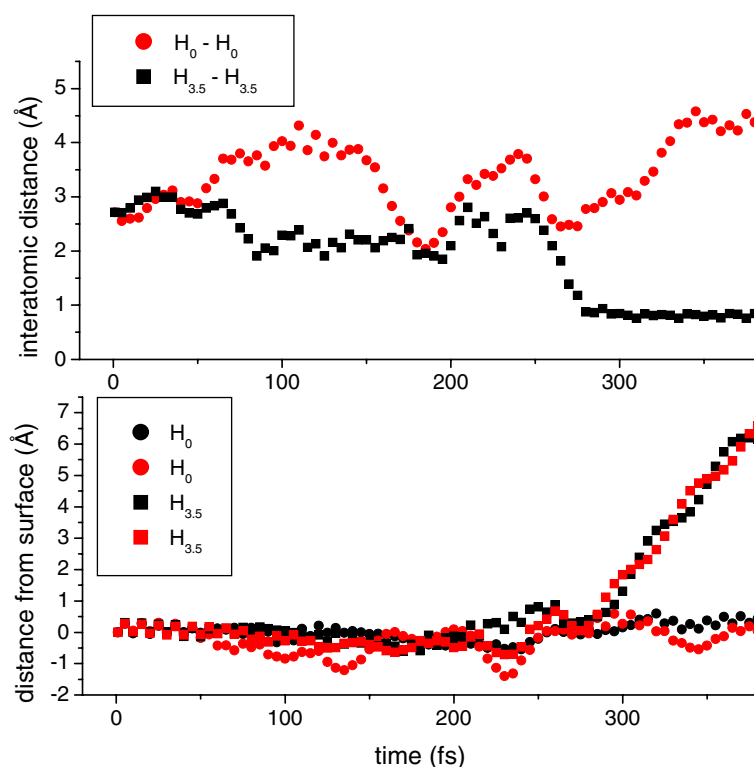


**Figure 3.** The simulation trajectories of the molecule-forming hydrogen (hollow symbols in figure 2(b)), for 3.5 eV initial kinetic energy of the bombarding  $\text{Al}^{1+}$  ion.

When the  $\text{Al}^{1+}$  ion is assigned 0 eV initial kinetic energy, it will move towards the surface due to attraction. Investigating the subsequent ion–surface collision in more detail, an adsorption induced surface relaxation is observed. A single-point-energy calculation in the gradient corrected approximation (GGA) for the initial and final (after 0.5 ps) configuration of the system shows a decrease in energy by 8.4 eV. However, the internal energy of the system is here conserved, meaning that there is a corresponding increase in kinetic energy. Energy supplied to a surface through an ion surface collision may enable bond breaking and surface migration. The kinetic energy in this case is evidently not enough to initiate surface migration to an extent to enable hydrogen molecule formation.

As the kinetic energy of the bombarding ion is increased to an initial energy of 3.5 eV, more surface migration is observed. This is exemplified in figure 4(a), comparing the interatomic distance during the simulations between the two surface hydrogen atoms marked in figures 1 and 2: the interatomic distance decreases around 0.25 ps, leading to bonding and molecule formation. The subsequent molecule desorption from the surface is illustrated in figure 4(b), comparing the hydrogen atom–surface distance during the simulations. Also here, surface relaxation upon the Al adsorption (and hydrogen desorption) is observed. The calculated (single point energy calculation, GGA) potential energy difference between the initial and final configuration is 10.4 eV, which is 2 eV higher than the previous configuration where there is no change in surface composition upon collision. This may indicate a reaction towards a potential energy minimum of the system upon molecule formation and removal from the surface, and is consistent with entropy increase as the system approaches equilibrium. However, a study of the oscillation in energy for the last 0.1 ps of the simulation shows a standard deviation from the average kinetic energy of 1.11 and 0.94 eV for the case of 3.5 and 0 eV initial  $\text{Al}^{1+}$  energy, respectively. A corresponding fluctuation can therefore also be expected for the potential energy.

The results presented above can be understood based on thermodynamics. The Gibbs free energy is the thermodynamic potential of the thermal–isobaric constant- $NPT$  ensemble, where  $N$  is the number of particles,  $P$  is the pressure, and  $T$  is the temperature, respectively. Because of the boundary conditions (constant  $NVE$ ), the appropriate thermodynamic potential for the microcanonical ensemble can be reduced to the entropy [21], and hence corresponds to the function that has its extreme value at thermodynamic equilibrium. Consequently, as the



**Figure 4.** The interatomic distance during the simulation, between the two surface hydrogen atoms marked with hollow symbols in figure 1 and 2.

simulation system evolves towards equilibrium, an entropy increase is expected. The results of the simulation can be explained by an activation energy for bond breaking and surface migration being supplied in the 3.5 eV initial kinetic energy simulation, in contrast to the kinetic limitation observed in the low energy simulation. The migration enables  $H_2$  formation. It is straightforward to appreciate that a solid to gas transformation corresponds to an increase in entropy.

The notion presented here that unintentional incorporation of residual gas in thin films can be affected by ion bombardment is highly relevant for all deposition techniques including low energy ions, such as plasma assisted CVD [22] and PVD. Furthermore, in a recent study of the effect of gas pressure on the ion energy in cathodic arc plasma,  $Al^{1+}$  was found to be the most abundant ion at elevated oxygen pressure. This is exemplified in figure 5, with the fraction of the ions having an energy of  $>3.5$  eV being about 90%. Film depositions of  $Al_2O_3$  in the same system [23] showed very low hydrogen incorporation ( $<0.25$  at.%), which supports the notion presented here of affecting hydrogen incorporation by ion bombardment.

In summary, the effect of ion energy on surface reactions has been investigated for collisions between an  $Al^{1+}$  ion and a gibbsite surface. *Ab initio* MD within density functional theory was used for this purpose. For 0 eV initial kinetic energy of  $Al^{1+}$ , no change in surface composition was observed. An increase in energy to 3.5 eV showed extended surface migration of hydrogen, with subsequent  $H_2$  formation and desorption. These results may be understood by thermodynamic principles, where the kinetic energy transferred to the surface facilitates bond breaking and migration, to enable an increase in entropy through gas formation. These

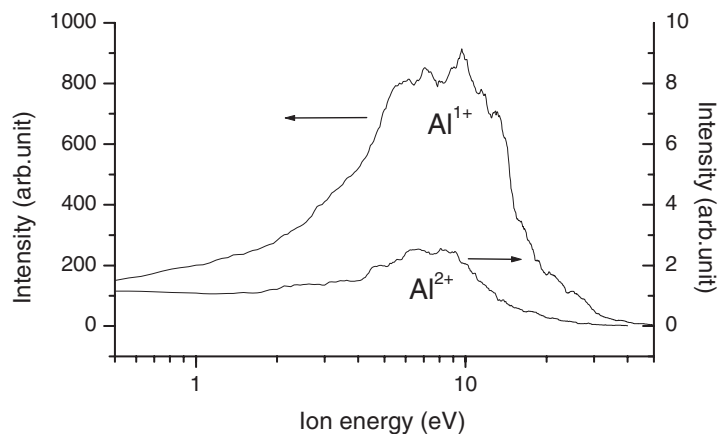


Figure 5. Ion energy distributions for  $\text{Al}^{1+}$  and  $\text{Al}^{2+}$  in an Al arc plasma at  $8 \times 10^{-3}$  Torr  $\text{O}_2$ .

results are of fundamental importance for an increased understanding of thin film growth through the correlation between ion energy and film composition. They may also indicate a pathway to affect impurity incorporation during film growth.

## References

- [1] Schneider J M, Sproul W D, Voevodin A A and Matthews A 1997 *J. Vac. Sci. Technol. A* **15** 1084
- [2] Zhu S, Wang F, Lou H and Wu W 1995 *Surf. Coat. Technol.* **71** 9
- [3] Serra E, Benamati G and Ogorodnikova O V 1998 *J. Nucl. Mater.* **255** 105
- [4] Sosniak J 1966 *J. Vac. Sci. Technol.* **4** 87
- [5] Schneider J M, Anders A, Hjärvarsson B, Petrov I, Macák K, Helmersson U and Sundgren J-E 1999 *Appl. Phys. Lett.* **74** 200
- [6] Gitzen W H 1970 *Chemical Properties of Alumina* (Columbus, OH: American Ceramics Society) p 103 (Special Publication No. 4)
- [7] Schneider J M, Larsson K, Lu J, Olsson E and Hjärvarsson B 2002 *Appl. Phys. Lett.* **80** 1144
- [8] Schneider J M, Hjärvarsson B, Wang X and Hultman L 1999 *Appl. Phys. Lett.* **75** 3476
- [9] Chen Y-P 2002 *J. Nucl. Mater.* **303** 99
- [10] Rosén J, Schneider J M and Larsson K 2005 *Solid State Commun.* **134** 333
- [11] Dörre E and Hübner H 1984 *Alumina* (Heidelberg: Springer)
- [12] Schneider J M, Anders A, Brown I G, Hjärvarsson B and Hultman L 1999 *Appl. Phys. Lett.* **75** 612
- [13] Oks E and Yushkov G 1996 *Proc. 17th Int. Symp. on Discharges and Electrical Insulation in Vacuum (Berkeley, CA)* p 584
- [14] Rosén J, Schneider J M and Larsson K 2005 *J. Phys. Chem. B* **108** 19320
- [15] Payne C M, Teter M P, Allan D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* **64** 1045
- [16] Verlet L 1967 *Phys. Rev.* **159** 98
- [17] Tuckermann M E 2002 *J. Phys.: Condens. Matter* **14** R1297
- [18] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [19] Kleinman L and Bylander D 1982 *Phys. Rev. Lett.* **48** 1425
- [20] Wang X-G, Chaka A and Scheffler M 2000 *Phys. Rev. Lett.* **84** 3650
- [21] Pearson E M, Halicioglu T and Tiller W A 1985 *Phys. Rev. A* **32** 3030
- [22] Seaward K L, Turner J E, Nauka K and Nel A M E 1995 *J. Vac. Sci. Technol. B* **13** 118
- [23] Rosén J, Mráz S, Kreissig U, Music D and Schneider J M 2005 *Plasma Chem. Plasma Proc.* at press