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Surface Science 600 (2006) 2587–2593
SURFACE SCIENCE
www.elsevier.com/locate/susc

Deformation of slow liquid and solid clusters upon deposition: A molecular-dynamics study of Al cluster impact on an Al surface

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Received 14 September 2005; accepted for publication 19 April 2006
Available online 11 May 2006

Abstract

Using molecular-dynamics simulation, we investigate the self-deposition of Al_n clusters ($n < 4000$) on an Al substrate at velocities below the velocity of sound. Both cold crystalline and hot liquid clusters are studied. We examine the cluster deformation after impact on the surface, which we quantify by its height and base radius. At a given cluster velocity, the shape of deposited crystalline clusters is rather independent of the cluster size; only at small cluster sizes, $n \lesssim 40$, the clusters are less strongly deformed. With increasing cluster size, liquid clusters are more strongly deformed than crystalline clusters. Faster projectiles become more strongly flattened by the deposition process. Even clusters depositing with vanishing velocity show a finite deformation, which is considerable for smaller clusters. At large cluster speed, clusters penetrate deeper into the (1 0 0) surface than into the (1 1 1) surface and also deform more strongly.

Keywords: Cluster deposition; Molecular dynamics; Wetting; Growth

1. Introduction

In recent years, the interaction of clusters with surfaces has received increased attention. In particular, the deposition of size-controlled clusters on surfaces has found widespread interest [1]. By controlling the cluster size and the impact energy, it is possible to create nano-scale structures on the surface [2–4]. Such nano-structured materials are of interest for example with respect to their optical properties, and find applications in the emerging fields of plasmonics, where the plasma resonance of the electron gas of a metallic nanoparticle is employed [5–8]. Further applications in the fields of nanoelectronics and nanophotonics are beginning to be investigated [9–11]. When slow clusters are deposited on surfaces ('soft landing') they may deposit intact on the surface [12] and the resulting 'supported clusters' form a research field of its own right for studying the properties of clusters in contact with the substrate [1,13]. Thin-film deposition methods using cluster beams have been studied and the resulting film quality has been assessed in terms of cluster velocity and size [2,14–16]. But also in conventional pulsed-laser deposition methods, the depositing beam consists not only of atoms but also of smaller and larger clusters ('droplets'), which originate from the laser ablation process or may possibly have agglomerated in the dense ablation plume [17]. In all the applications mentioned above, a knowledge of the shape of the deposited cluster is relevant.

Harbich [16], extending previous ideas by Averback and coworkers [18] discusses various scenarios occurring after cluster impact on a surface as a function of the so-called reduced energy per atom

$$\epsilon = \frac{E/n}{E_{\mathrm{coh}}}. \tag{1}$$

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doi:10.1016/j.susc.2006.04.024

Here E is the total kinetic impact energy of the cluster, n the number of its constituents and E_{coh} the cohesive energy of the target. In the case where cluster and target consist of the same material, these references define for $\epsilon \lesssim 0.1$ the regime of 'soft landing', where the cluster sticks at the impact point and keeps its identity; the collision-induced deformation is only elastic. A closer discussion shows that – due to the cluster–target adhesion forces – small clusters ($n \lesssim 100$) will as a rule not soft-land but deform, even at vanishing impact energies. For $\epsilon \lesssim 1$, plastic deformation of the cluster upon impact will occur; this regime has also been called 'ballistic deposition'. At even higher energies, fragmentation of the cluster and implantation into the target will occur.

Experimental studies concentrated on the deposition of smaller metal clusters ($n \lesssim 100$) on graphite, and here on the regime of unfragmented deposition (soft landing or ballistic deposition) [19–22]. Here, due to the special nature of the graphite surface, a further regime was found, in which the deposited cluster creates a defect in the graphite surface to which it is pinned. This so-called 'pinning regime' is interesting since it prevents the diffusion of deposited clusters on the surface and thus prepares well-defined isolated supported clusters [23].

Yeadon et al. [24] experimentally observed the phenomenon of 'contact epitaxy', where sufficiently slow crystalline clusters aligned epitaxially with a crystalline substrate surface. Molecular-dynamics simulations [24,25] revealed that the alignment arises from mechanical relaxation of the highly-stressed interface formed upon initial contact. At higher energies, Vandoni et al. [26] determine the degree of defect production, implantation and cluster fragmentation for small Ag_n clusters ($n = 1$–19) deposited on a Pd(1 0 0) surface. These experiments were later analysed quantitatively using molecular-dynamics simulation, and the above measurements could be quantitatively reproduced [27]. Experiments comparing the deposition behaviour of liquid and solid clusters have to our knowledge not been performed up to now, even though they are relevant for an understanding of the deposition of liquid clusters in pulsed-laser desorption experiments.

In the present paper, we shall study the deformation of a cluster upon deposition. The case of self-bombardment of an Al cluster on an Al substrate will be studied. The cluster is assumed to be initially spherical with a radius R in the range of 0.3–2.5 nm; it hence contains between $n = 13$ and $n = 4000$ atoms. Cluster velocities below and up to the speed of sound of Al, $v_s \cong 5$ km/s, are investigated. This restriction has two reasons: (i) for higher speeds, the cluster will produce increasing damage in the substrate, and intermixes with it, and hence its identity and shape are destroyed. (ii) This velocity regime is the one used in applications like soft cluster landing and – with some exceptions – thin-film deposition.

In particular, we want to study differences in the deposition behaviour of cold and hot clusters. Depending on the cluster formation process, the cluster can reach the substrate with different temperature. It might be expected that the hot liquid cluster will deform in a different way than a cold crystalline cluster when bombarding the substrate with identical velocity. Note that, for instance, an Al atom with velocity 1 km/s has a kinetic energy of 140 meV/atom, which is comparable to the thermal kinetic energy $(3/2) \cdot kT = 129$ meV/atom at $T = 1000$ K. Furthermore, the higher atom mobility in the liquid state might influence cluster deformation.

2. System and method

We perform an exemplary case study on the self-deposition of Al_n clusters on an Al substrate. We selected this material, since here a well-documented and tested interatomic interaction potential is available [28], which describes not only the zero-temperature properties of the crystalline state – this is quite usually the case for all metal potentials – but also the properties of liquid Al, and in particular the melting transition. Here not only the melting temperature of $T_m = 933.6$ K is reproduced, but also thermal properties such as the latent heat and volume change upon melting. The interatomic interaction potential has a many-body form, which reproduces well the cohesive and elastic properties of Al, as well as the surface energies of the low-indexed crystal faces, point-defect energetics, etc. For reference, we note the cohesive energy $E_{\mathrm{coh}} = 3.39$ eV and the velocity of sound $v_s = 5.13$ km/s, calculated from the bulk modulus B and the mass density ρ via $v_s = (B/\rho)^{1/2}$. Note that the kinetic energy of an atom moving at the speed of sound is roughly identical to the cohesive energy, as is usually the case in metals.

The substrate is an Al crystal; in the simulations presented here, the crystal has a (1 1 1) surface, but reference calculations have also been performed for a (1 0 0) surface. We choose its size in accordance with the cluster size and velocity; the number of atoms used varies between 1.9×10^4 and 2.4×10^5 atoms. While the top surface is free, the other five boundaries use damping boundary conditions in order to mimic energy and momentum transport to the surrounding environment. To this end the outermost three monolayers are subject to a velocity-proportional damping force constructed according to Ref. [29].

The crystalline cluster is constructed by cutting a spherical atom configuration out of an fcc crystal; thus it has one central atom surrounded by completely filled coordination shells. Then it is allowed to relax radially to reduce its potential energy; however, we did not allow it to facet. The liquid cluster is constructed using the same procedure. Then it is heated to a high temperature $T > T_m$ using a velocity-scaling algorithm, and allowed to follow free dynamics for 10 ps. Its temperature is $T \cong 1000$ K. We studied clusters with sizes $n = 13$–4000 atoms. The clusters are then shot with a center-of-mass velocity v towards the surface. The time evolution is calculated using a standard molecular-dynamics code [30]. We follow the simulation until the time $t = 20$ ps.