Growth of Au Clusters on Amorphous Al_2O_3: Evidence of Cluster Mobility above a Critical Size

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We study the 3D growth of clusters during the deposition of Au atoms on amorphous Al_2O_3. By comparing transmission electron microscopy images of the growth with Monte Carlo simulations, we show that nucleation takes place on substrate defects, but that further stages of growth imply that clusters leave the defects after they have reached a given critical size, and diffuse. An interesting consequence of this property is that, in contrast to intuition, and in a certain range of size, larger clusters are more mobile than smaller ones in this system.

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Understanding the growth and behavior of metal clusters on an insulating substrate is of prime importance in widely different application fields. Indeed such clusters may be used as the active parts in catalysts [1] as well as in single-electron transistors [2]. They also represent the first stages of growth of ultrathin films, currently used in capacitors and magnetic tunnel junctions. In most cases, the final properties strikingly depend on the clusters distribution, in size and in space.

Cluster growth on oxides is well documented [1,3,4] and has been the subject of an intensive work since the end of the 1960s. Anyway, these studies have especially been focused on the nucleation regime, for which experimental results can be compared with a good panel of equations. It allows one to deduce the nucleation mode, sticking coefficients, and adsorption or diffusion energies of atoms. In comparison, the coalescence regime has often been neglected. In former studies, we have observed that Co and Au deposition by sputtering on amorphous Al_2O_3 leads to a partially organized cluster distribution hard to explain with classical models of growth [5,6]. By comparing transmission electron microscopy (TEM) micrographs of real deposits of Au on amorphous Al_2O_3 to Kinetic Monte Carlo Simulations (KMCS), we show here that nucleation takes place on substrate defects and that the order in cluster arrangement is acquired during a coalescence regime implying cluster motion. The superposition of these two observations indicates that clusters stand still when they are small and that they detach from defects and diffuse on the surface after they have reached a critical size.

It is now well known that the final appearance of a deposit often depends on surface defects, as they have an influence on both the nucleation and the diffusion of clusters, but the exact nature of these defects and the way they interact with atoms is the subject of active research. Haas *et al.* have shown that it is possible to extract activation energies for defect trapping by studying carefully the temperature dependence of the density of Pd islands grown on MgO (001) [7]. In other respects, Yoon *et al.* varied the density of surface defects in experiments of soft-landing Sb clusters on graphite and showed that defects reduce their diffusion coefficient [8]. The fact that defects can become imperfect traps when clusters grow, i.e., that they can release the clusters they have trapped above a given critical size, has been reported only in the case of defects on crystalline NaCl [9,10]. We think that Heinemann *et al.* [11] also observed such effects though they did not point it out: when depositing Au on α-Al_2O_3 at 650 °C, they obtained a very high cluster number density, characteristic of a nucleation on defects. Most of the time, clusters were motionless but they observed fast mobility events: it is probable that they observed the sudden release of clusters by defects. So we suggest that this behavior, observed on such different substrates as a crystalline oxide, a crystalline alkali halide, and an amorphous oxide could be a general property of clusters on defects.

Our paper proceeds in two stages. Using a simple model, we first show that clusters are released by defects during the growth. Then, in a discussion, we qualitatively evaluate the additional effects of the complexity of the substrate.

In our system, we checked whether nucleation is homogeneous or not by watching the effects of varying two growth parameters (in two different sets of experiments): (1) the temperature and (2) the deposition rate. Decreasing deposition rate and increasing growth temperature should have indeed the same effect in the case of homogeneous nucleation: decreasing cluster number density, in a range that can be estimated by KMCS. A constant cluster density, on the other hand, is proof that nucleation takes place on defects. We then controlled the motion of clusters during the coalescence stages of growth by preparing thicker deposits and recording their TEM images as snapshots of those stages.

Our samples were fabricated in the following way: a 27 Å thick amorphous Al_2O_3 layer was first deposited by sputtering on the carbon membrane of electron microscopy grids. The rms roughness of such a layer has been found by atomic force microscopy to be 0.2 nm. All samples for a given experiment were deposited at the same time, in an Alcatel 610 sputtering equipment from an Al_2O_3 target in rf magnetron mode. These grids were then submitted to either one of the following procedures. (1) Sputter deposition: study of the effect of temperature. Au was deposited in rf mode and a 41 Å thick covering layer of amorphous Al_2O_3 was then deposited. The final structure was Al_2O_3–41 Å/Au/Al_2O_3–27 Å/*a*-C. (2) Evaporation in a MBE equipment: study of the effect of deposition rate and of the evolution with thickness. The grids were kept under nitrogen atmosphere before being placed in the MBE equipment. Au was then evaporated at room temperature and the samples prevented from evolution by the deposition of a 25 Å thick Al layer oxidized in air. TEM observations were performed using a Topcon 002B operating at 200 kV. Images were then binarized using the software OPTIMAS 6.0. We estimate that the error on the cluster density and diameter due to this process does not exceed ±10% [5].

We then matched the TEM images with images of deposits simulated by KMCS. KMCS have shown their ability to reproduce the first stages of epitaxial metal growth [12]. In the case of granular growth, more complex phenomena are present such as cluster diffusion and coalescence, so KMCS have until now been used only to simulate the stage of nucleation and extract values for the diffusion energy of adatoms [4]. We have developed a new kind of KMCS, which can simulate the whole film growth, from nucleation to percolation [13], with only a few free parameters. Our Monte-Carlo simulations derive from those developed by Jensen [14]. We simulated the amorphous surface by a 2D lattice, with a hexagonal symmetry to reduce anisotropic effects, and the lattice parameter of Au so that there is a good correspondence in the simulations between the number of atoms in clusters and their diameter. It gives a site density of 9.59×10^{14} sites/cm^2. The hypotheses we used are the following:

(i) Atoms are sent randomly onto the surface with a constant deposition rate F.

(ii) Atoms can diffuse on the surface following a classical Arrhenius law $\tau = \nu_0^{-1} \exp^{E_d/kT}$, where τ is the mean time between two jumps, ν_0 the attempt frequency (10^{12} s^{-1}), E_d the diffusion activation energy, k the Boltzmann constant, and T the temperature.

(iii) If defects are present, they are put randomly on the lattice, and perfectly trap atoms.

(iv) Clusters have the equilibrium shape of Au on Al_2O_3. This shape is almost spherical, with a wetting angle between the cluster and the substrate of 40° [3].

(v) If clusters diffuse on the substrate, the diffusion verifies the relation $D_N = \frac{D_0}{N^\gamma}$, where D_N is the diffusion coefficient of a cluster containing N atoms, D_0 the diffusion coefficient of a single atom, and γ a parameter. This empirical law well applies to describe the movement of 3D clusters on a surface [15].

(vi) When two clusters come into contact, the coalescence phenomenon includes in practice several diffusion processes [16,17]. For the sake of simplicity, we assume that diffusion at the cluster surface dominates. In that case, they coalesce in a time given by [18] $\tau_{\text{coal}} = \frac{R^4}{B}$, where R is the radius of the smaller cluster and B a parameter. Coalescence in our simulations is a "binary" process: when two clusters come into contact, they stay aside during τ_{coal} and then coalesce instantaneously.

We first present the results of the effect of temperature on cluster distribution (samples prepared by sputtering). 4 Å of Au were deposited at room temperature and at 400 °C, at a deposition rate of 0.29 Å/s. We can see in Fig. 1 TEM plan views after treatment of the images. The densities of clusters are 4×10^{12} and 3.8×10^{12} clusters/cm^2 for the two respective temperatures. If the nucleation were homogeneous, i.e., without nucleation on defects, KMCS show that the cluster density should vary by more than an order of magnitude between room temperature and 400 °C. The observed low variation of the cluster density with deposition temperature shows that nucleation occurs on the surface defects of sputtered Al_2O_3. This conclusion is confirmed by the experiments where the deposition rate was varied (samples prepared by evaporation). A nominal thickness of 2 Å of Au was deposited at deposition rates varying from 0.33 Å/mn to 5.25 Å/mn: within experimental uncertainty, the cluster densities obtained for the different rates are the same, whereas KMCS predict a cluster density variation of more than a factor 2 in the absence of defects (Fig. 2).

We also varied the thickness of the MBE samples in order to obtain experimental snapshots of the different stages of growth, to be compared with the different stages of the Monte Carlo simulations. The evolution of the growth between 2 and 10 Å of nominal thickness is presented in Fig. 3. To simulate the deposition, we first supposed that defects are perfect traps for atoms and that clusters stay motionless on the defects where they have been created. In such a case, the only free parameters of the simulation are the concentration of defects and the parameter B governing the coalescence time. We chose a defect concentration that reproduces the cluster density and the size histogram of the 2 Å sample. For such a thickness, all defects are saturated [19], but some clusters on neighboring defects have already coalesced. That is why the density of

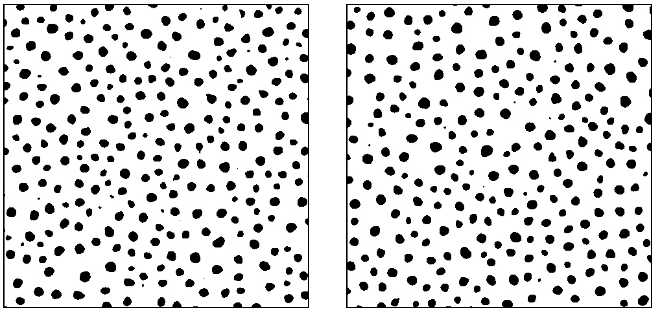

FIG. 1. Binarized TEM plan views of multilayers Al_2O_3–41 Å/Au–4 Å/Al_2O_3–27 Å/*a*-C deposited at room temperature (left) and at 400 °C (right) (80 × 80 nm). A nominal thickness of 4 Å is deposited. The mean cluster diameter is about 25 Å.

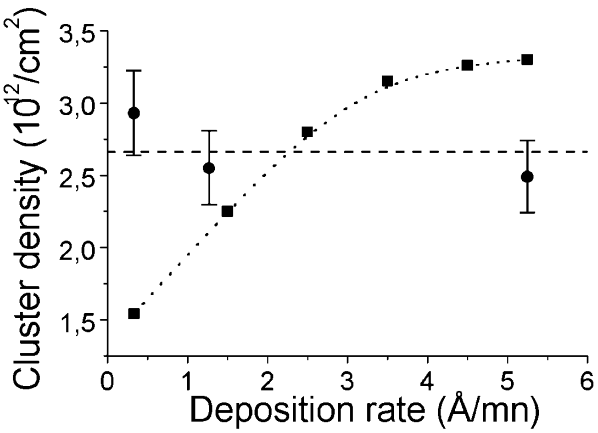

FIG. 2. Density of clusters for MBE samples with a nominal thickness of 2 Å of Au deposited at various deposition rates (round dots). The mean diameter of the clusters obtained is 2 nm. Squares come from a Monte Carlo simulation assuming that homogeneous nucleation occurs. Dashed and dotted lines are guides to the eyes.

defects is slightly higher than the cluster density: defects density and B values were, respectively, 3.2×10^{12} cm^{-2} and 2.4×10^{-36} m^{4}s^{-1}. We can also deduce from a comparison between KMCS and the MBE experiments a higher limit for E_d as atoms must have time to diffuse enough to reach the defects, even at the highest deposition rate. It gives $E_d < 0.4$ eV.

There are significant differences between the real evolution of the sample (Fig. 3, experiment) and the simulated one (Fig. 3, simulation 1). It can be more clearly seen when comparing size histograms for the 10 Å sample and for the simulation 1 (Fig. 4): simulation predicts a growth with a very narrow size distribution centered around 5 nm. In the experiments, there is a smaller density of larger clusters and a significant population of small renucleated clusters. A hypothesis is therefore that a cluster could leave the defect where it was created, and let it open to new nucleations. To check this hypothesis, we have developed a simple model, where all clusters leave the defects above a given size, and diffuse on the substrate, following the laws presented above. KMCS shows that the growth can be well fitted with $E_d = 0.36$ eV, $\gamma = 2$, a defect density of 3×10^{12} cm^{-2}, and clusters leaving the defects when they have more than 600 atoms, i.e., a diameter of about 3 nm (simulation 2 in Figs. 3 and 4).

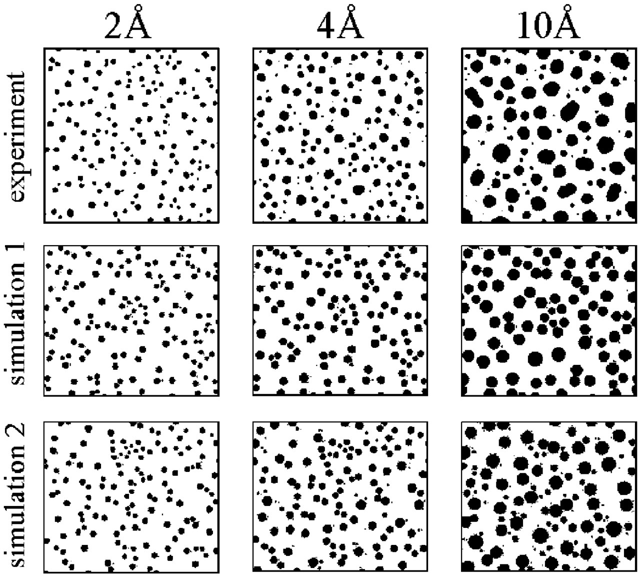

FIG. 3. Images of the MBE deposited samples and of Monte Carlo simulations. From left to right: a nominal thickness of 2, 4, and 10 Å is deposited. From top to bottom: TEM images of MBE samples after binarization; simulation 1, assuming that clusters stay motionless on the defects; simulation 2, assuming that clusters can trap off from defects above a given size. The size of the field of view is 80 × 80 nm in the TEM images and 80 × 70 nm in the simulations.

Some of the defects probably come from the implantation of Ar$^+$ ions during sputtering (we recall that even with the MBE deposited samples, the substrate is prepared by sputtering). Energy dispersive spectroscopy of x-ray (EDX) has indeed shown the presence of Ar in the layers. This origin of the defects would also explain why the density of clusters is slightly higher in the sputtered Au samples than in the MBE deposited samples: new defects are probably created in Al_2O_3 during the Au deposition by sputtering.

The variety of adatom sites on an amorphous substrate suggests that there should be a variety of defect sites so the trapping energy of defects should not have a single value. We checked this by investigating the early stage of the growth at different temperatures. In the curves of the cluster number density versus temperature, the existence of only one type of trap should appear as a plateau, as shown by Haas *et al.* [7]. When depositing 2 Å of Au by sputtering at 20, 200, 400, and 600 °C, at a rate of

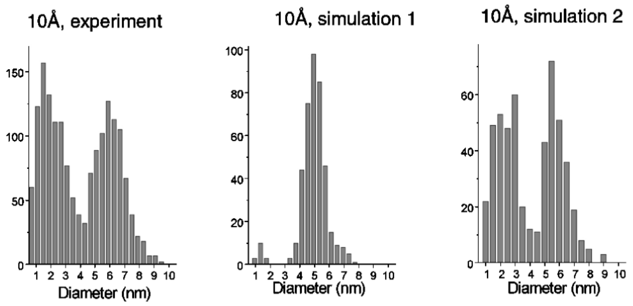

FIG. 4. From left to right: size histogram of the MBE sample, where a nominal thickness of 10 Å was deposited; size histogram of the simulation 1, assuming that clusters stay motionless on the defects; size histogram of the simulation 2, assuming that clusters can trap off from the defects above a given size. In histograms extracted from simulations, we removed clusters whose diameter is below 1 nm, in order to reproduce the cutoff frequency of the contrast enhancement treatment of the TEM image. The MBE histogram comes from a surface of about 100 000 nm^2. The simulated histograms are the sum of five runs.

0.29 Å/s, we obtained a cluster density of, respectively, 4.7, 3.9, 2.7, and 1.7×10^{12} cm^{-2}. If the absence of a steep decrease is a new proof of nucleation on defects, the absence of a plateau, however, confirms the existence of several strengths of traps. If we compare our data with the curves calculated by Haas *et al.* [7], it thus appears that (i) as the density already decreases between 20 and 200 °C, some of the traps have a low trapping energy (<0.8 eV), and (ii) as the density does not sharply drop between 400 and 600 °C, some other traps have a high trapping energy (>1.6 eV).

Of course, there are no reasons why the different defects would release the clusters at the same size. One should expect that high-trapping energy defects are better traps for clusters than low-energy defects, as is the case for atoms. So the reality of the growth is more complicated than the simple model assumed in the KMCS: clusters are actually released over a distribution of sizes. It has important consequences for the diffusion coefficient of 3D clusters on such a surface. In the case of a homogeneous substrate surface, it is a monotonic decreasing function of cluster size [15]. On a substrate with one type of defects, the diffusion coefficient as a function of size abruptly increases from zero to a finite value at a given critical size. On a surface with a range of defects as the amorphous Al_2O_3, this increase will be progressive. Experiments of cluster beam deposition on such a surface could confirm it [8,20].

In conclusion, we have developed novel Monte Carlo simulations, including atomic diffusion, nucleation on defects, and cluster coalescence. Their interest is to be able to simulate with simple hypotheses the whole granular growth, from nucleation to percolation, which has never been done. We applied them to simulate the Au deposition on amorphous Al_2O_3. We first demonstrated that nucleation occurs on the defects of the sputtered Al_2O_3. A precise study of the deposit evolution with thickness shows an anomaly in the coalescence regime. It can be well explained if assuming that clusters leave the defects where they have been created and diffuse on the substrate. This behavior has previously been found in the case of NaCl [9,10]. We think that experiments of Heinemann *et al.* on α-Al_2O_3 can be reinterpreted as another example of this phenomenon [11]. So we suggest that this property, observed on such different substrates as a crystalline oxide, a crystalline alkali halide, and an amorphous oxide could be a general property of clusters on defects.

We have then shown that in the case of amorphous Al_2O_3, there is a distribution in the trapping energy of defects and we have considered that different defects should release clusters at different sizes. An important consequence of that concerns the diffusion properties of 3D clusters on a surface. In the case of a homogeneous substrate surface, such as a defect-free crystalline surface, cluster diffusion is a monotonic decreasing function of cluster size [15]. In the case of a surface having a distribution of defects, such as that of an amorphous substrate, one should expect a more complicated behavior. In the size range where clusters are progressively released by the trapping defects, effective cluster diffusion should indeed *increase* with cluster size.

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