Modeling of film growth by cluster deposition: The effect of size and energy

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The density of cluster-assembled thin films depends heavily on the size of the deposited clusters as well as the energy with which they impact the substrate. Using molecular-dynamics simulations we have quantitatively studied variations in the density of thin films grown by deposition of clusters, with diameters between 1 and 9 nm, and at energies ranging from 2 meV to 10 eV per cluster atom. A model explaining the behavior of smaller clusters is presented, and a threshold limit in cluster size, where deviation from this model occurs, is determined. The deviation is shown to be due to a lessened sintering between clusters.

I. INTRODUCTION

The use of nanocluster deposition has recently become an interesting prospect for the growth of structured thin films.[1,2] Due to their inherent nanoscale structure and properties, size-selected clusters are ideal building blocks for new materials with tailored properties. Cluster deposition is, however, a complex process, where even the slightest changes in cluster size or deposition energy can result in crucial differences within the final structures.[3,4] A detailed understanding of mechanisms during cluster deposition is imperative if nanoclusters are to be of use in thin-film technology.

Several outcomes in thin-film qualities have been experimentally achieved for many single elemental and binary metal systems through the variation in deposition parameters during film growth by cluster deposition. Epitaxial alignment, and therein a dense single-crystal structure, has been achieved with deposition of cluster with sufficiently small sizes.[5,6] High deposition energies have similarly resulted in dense thin films with good adhesion and mechanical durability, even though larger clusters have been used. At lower deposition energies, large clusters will, however, form a porous film with poor mechanical qualities.[3,4,7] Although these films are found to be stable at room temperature,[7–9] they are not very durable to mechanical stresses.

In this work we have simulated the growth of thin films by deposition of multiple Cu clusters on a Cu surface. Films were grown for various sizes of clusters and with different deposition energies, after which densities of the resulting films were determined. The effect of surface energy, released during cluster impact, as well as that of increased deposition energy, on resulting thin-film properties, was ascertained.

II. METHOD AND SIMULATIONS

Classical molecular-dynamics simulations were used to deposit a sequence of 50 equisized Cu nanoclusters on a smooth (100) Cu substrate. The substrate size, in its lateral directions, was approximately three times larger than the diameter of the clusters, and its thickness was chosen such that it would be large enough to allow for the energetic deposition of clusters without too much immediate energy loss through the borders of the simulation cell. The simulation cell was given periodic boundaries in the lateral directions of the substrate, whereas the bottom layer of the substrate was fixed, with temperature scaling applied to a few atomic layers above this. By these means, both a larger surface of a bulk substrate, as well as a larger deposited film, could successfully be mimicked.

Cu atom interactions were described with the use of the embedded-atom method potential of Foiles.[10,11] The temperature control algorithm of Berendsen *et al.*[12] with a time constant of 300 fs was used to stabilize the temperature at the borders and the bottom of the simulation cell. All simulations were performed at a temperature of 300 K.

The clusters were given the shape of Wulff polyhedra,[13] with the dimensions of each cluster volume optimized to the configuration of minimum surface energy.[14] Other potentials and initial cluster shapes have previously been tested, for which no significant differences were observed.[15,16] Film growth with each cluster size was repeated up to four times in order to collect sufficient statistics.

Cluster deposition was carried out by giving each cluster a velocity in the direction of the substrate corresponding to the specific deposition energy under study. The film structures were then relaxed for 100 ps before the next clusters were deposited on top of them. Between each impact the substrate and any previously deposited film structure was translated a random distance through the periodic boundaries of the simulation cell. In this way impact points for any future clusters were random with respect to the previously deposited structure. All clusters were rotated to random orientations prior to deposition.

The density of the thin films was estimated by numerically calculating the amount of atoms in planar segments throughout the film and comparing the mass of these atoms to the volume of the segment. For each film the topmost 15% of the film thickness was left out in order to neglect the density-lowering effect of surface roughness.[3]

III. RESULTS AND DISCUSSION

The main results, concerning the effect of cluster size on film density, can be seen in Fig. 1, which shows the average density of the deposited thin films for different cluster sizes. The results of the figure are predominantly from low-energy deposition (5 meV/cluster atom), although some results for deposition of Cu_{5882} clusters at slightly different energies
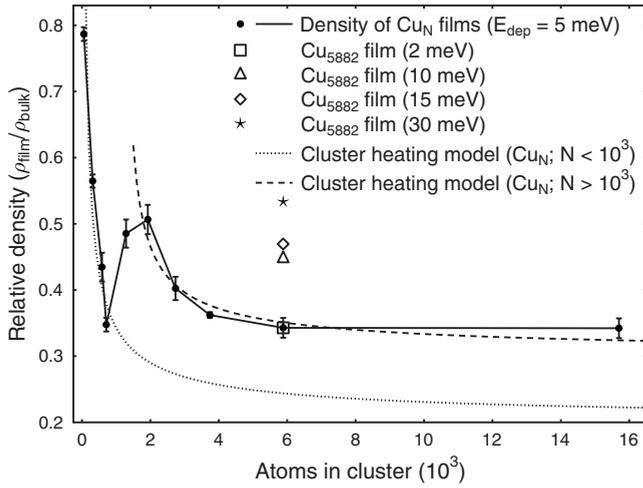
FIG. 1. Density of thin films grown by low-energy deposition (5 meV/atom) of various sized clusters as a function of the cluster size. Densities of films grown with Cu_{5882} clusters at energies of 2, 10, 15, and 30 meV/atom are also included. Densities decrease sharply up to a threshold value in cluster size, where the results are shifted toward higher densities. This shift is due to a closer packing of clusters that no longer stick to each other as easily when their size increases. The dotted line is a fit based on the model for cluster heating at impact, which applies to growth with clusters that have less than 1000 atoms. The dashed line shows how the density of films grown with larger clusters, above the threshold value, follows the same trend as the cluster heating model if the model is shifted toward higher densities.

have been incorporated into the figure in order to illustrate how deposition energy will affect film density.

A. Cluster heating

In order to explain the results, for cluster sizes of below 1000 atoms, a model of cluster heating at impact has been applied. According to the model, which has been presented in an earlier study,[17] binding energy is released as clusters impact on surfaces, due to the loss of surface area, and therefore surface energy of the cluster. This energy will predominantly go toward a heating of the cluster and its local surroundings,[15,16,18] and will therefore promote a reorganization of the cluster atoms, leading to, e.g., an epitaxial arrangement, according to the underlying substrate or any previously deposited clusters,[14] or a sintering of the clusters.

The cluster heating model gives an estimate of the amount of energy released, due to the loss of surface area,[14] when a cluster lands on a surface, as

$$\Delta E = 2\gamma A, \tag{1}$$

where γ is the surface energy and $2A$ is the surface area lost upon adsorption.

The total area lost when two clusters collide can be estimated by approximating a cluster by a sphere and the surface area A by its segment, with a height h, giving $A = 2\pi rh$, where r is the radius of the cluster. In the previous model,[17] for a cluster landing on a smooth surface, h was estimated as the interaction range of the atoms, and set to be equal to one

lattice constant, i.e., $h = a$. For the case of two clusters colliding, this interaction length will be shorter due to the curvature of the clusters. If the clusters are perfectly spherical, h should take a value approximately half of what it was in the previous model, giving $h = a/2$.

The increase in temperature resulting from the release of surface energy, ΔT, can be estimated from the relation

$$\frac{3}{2}Nk_B\Delta T = \frac{\Delta E}{2}, \tag{2}$$

where N is the number of atoms in the cluster, $N = \frac{16\pi r^3}{3a^3}$, and the released energy is divided by 2 due to the equipartition theorem. Combining the previous equations and solving for the change in temperature, we get

$$\Delta T = \left(\frac{\pi^2}{18}\right)^{1/3}\frac{\gamma a^2}{k_B}N^{-2/3}. \tag{3}$$

The density of a cluster-assembled thin film will increase if temperature is increased due to an increased sintering of clusters at elevated temperatures,[8] and one can therefore make the rough assumption that $\rho \propto \Delta T$, where ρ is the relative density of the film. Using this relation, Eq. (3) can be expressed as

$$\rho = \Lambda\frac{\gamma a^2}{k_B}N^{-2/3} + \rho_0, \tag{4}$$

where Λ, into which the first factor of Eq. (3) has been incorporated, and ρ_0 are fitting parameters. In Fig. 1 the model of cluster heating has been fit to the data points of clusters with sizes below 1000 atoms using values of $a = 3.61$ Å and $\gamma = 1.29$ J/m^2 (Refs. 11, 17, and 19), and fitting parameters $\Lambda = 0.0012$ K^{-1} and $\rho_0 = 0.2$, giving a fairly good agreement with the simulated values for cluster with less than 1000 atoms. The value of ρ_0, the lowest density attainable in the model, curiously enough, corresponds to the relative packing density of newly fallen snow,[20] a deposition process which is very similar to that of cluster deposition.

Further proof of the densifying effect of cluster heating is given in Fig. 2, where the distribution of relative distances between adjoining clusters is shown for films grown with different cluster sizes at a deposition energy of 5 meV/atom. The inset in Fig. 2 illustrates the intercluster distance, d, and the diameter of a cluster, $d_{cluster}$—values that were used in determining the relative distances between clusters. The distributions of distances for the smaller clusters are rather uniform, with distances between the centers of adjoining clusters also being very much smaller than the combined radii of two pristine clusters, i.e., a relative distance of 1.0. A greater amount of energy per atom in the cluster is released for a smaller cluster, which causes a greater deformation and more advanced sintering than for the larger clusters.

The validity of the cluster heating model has been shown for several metals in the case of single clusters impacting on smooth surfaces.[17] A similar behavior portrayed by all metallic clusters impacting on pristine surfaces hints toward a similar growth mechanism for deposition of small clusters of all of these materials. The precise limit at which the behavior deviates from that of the cluster heating model is, however,
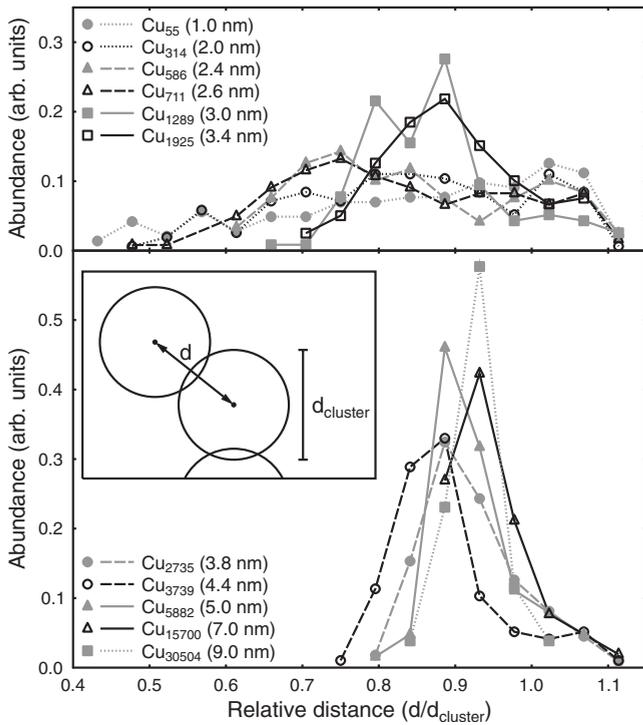
FIG. 2. The distribution of relative distances between adjoining clusters in thin films assembled with various cluster sizes. The deposition energy during film growth was 5 meV/atom. Distances between the centers of each cluster are normalized by twice the radius, in other words, by the diameter of the clusters. The inset shows a schematic of the difference between the intercluster distance, d, and the diameter of a cluster, $d_{cluster}$.

very material dependent and cannot be predicted without further studies.

B. Large clusters (above 1000 atoms)

The discrepancy of the cluster heating model, for clusters containing more than 1000 atoms, can be explained by Fig. 2, as the distributions for larger clusters grow sharper and their peak values shift closer to a state where not much overlapping of clusters occurs. The main reason for the failure of the cluster heating model at cluster sizes above 1000 atoms is an effect of this lesser overlapping or sintering of the clusters. As the degree of sintering diminishes with cluster size, clusters can no longer stick as easily to each other. This is proven by Fig. 3, where the average contact angle, for clusters that are supported by only a single cluster, is plotted. This angle is defined in such a way that 90° corresponds to a situation where the two clusters are directly on top of each other, while at 0° they lie side by side. For the sake of clarity this is also illustrated in the inset of Fig. 3.

A sharp increase in the contact angle occurs after 1000 atoms is surpassed, which gives an explanation to the rapid increase in the density of films at these cluster sizes, observed in Fig. 1. If a cluster with less than 1000 atoms impacts a previously deposited cluster at a low angle, it will stick, leaving a large void below it. When clusters above this limit impact others at a low angle, they no longer stick, but
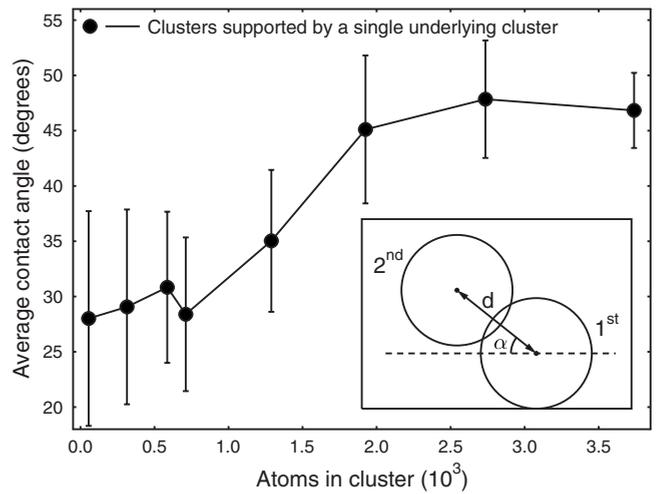
FIG. 3. The average angle of contact between clusters supported by a single underlying cluster and those supporting clusters as a function of the cluster size. The contact angle is defined as such that the angle between two adjoining clusters residing in the same horizontal plane is 0°, while the contact angle for a cluster directly on top of its supporting cluster is 90°. The inset shows a schematic of how angle, α, between a previously deposited cluster (1st) and a cluster deposited later (2nd), is defined.

rather continue onward, filling up the lower parts of the films, and thereby increase the average film density (since only clusters supported by a single underlying cluster are included in Fig. 3, this effect will lead to an increase in the average angle, as clusters which have continued onward will be supported by several underlying clusters). This effect causes a large increase in average film density for all of the films grown with larger clusters, even though densities continue to be gradually lowered, as a result of the lessened heating effect. The dashed line in Fig. 1 shows how the lowering in film density follows the cluster heating model at an offset caused by the lessened ability of clusters to stick at their original impact points.

C. Higher energies

If higher energies are introduced, by increasing the deposition energy of the clusters, cluster heating and sintering will increase and again result in a broader distribution of the relative distances between clusters in the film. Figure 4 illustrates this for the case of films grown by deposition of Cu_{5882} clusters at different energies. From the inset of the figure, which shows film density as a function of height, it is also clear that there are no major differences in the density distribution within the films but rather that the crucial difference causing an increase in film density is indeed a sintering of the clusters.

If deposition energies are still further increased, very high densities are attainable, as shown in Fig. 5. As deposition energies are increased by orders of magnitude, film densities eventually approach those of bulk copper. Figure 5 also illustrates the effect of surface roughness in lowering the average densities of the films, and the need for neglecting it, if correct densities are to be evaluated. The slightly lower den-
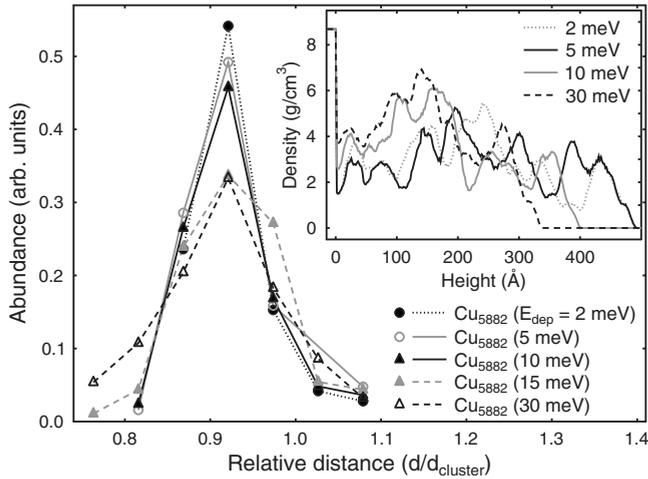
FIG. 4. The distribution of relative distances between adjoining clusters in films grown by deposition of Cu_{5882} cluster at various energies. A clear flattening of the distribution can be observed as deposition energies are increased. The inset shows density profiles for these films, where average density is plotted against distance from the surface of the substrate.

FIG. 5. The relative density of Cu_{586} cluster-assembled thin films as a function of the deposition energy per atom in the clusters. The dotted line shows the density for the entire film, whereas the solid line is the density calculated without the topmost 15% layer of the film. The difference between the two lines shows the effect that surface roughness has in a lowering of the average film density.

sity of films grown with a deposition energy of 10 meV/ atom, as compared to those grown with 5 meV/atom deposition energies, can be explained by an increase in sintering, and therefore a sticking at lower angles of the clusters deposited with higher energies.

In a previous study we have shown that for the case of copper, clusters of all sizes will melt completely upon impact once a limit in deposition energy per atom in the cluster is surpassed.[18] At deposition energies above this limit, approximately 0.6 eV/atom, thin-film growth by cluster deposition will result in films that have close-to-bulk densities, and most likely are single crystalline[3,4] and have good adhesive properties. As most metallic clusters behave similarly to copper clusters upon impact,[17] there is cause to believe that films with good mechanical qualities can be achieved with other metals at sufficiently high energies. The specific deposition energy limit at which this occurs is, however, material dependent.

IV. CONCLUSION

In conclusion, we have determined how the size and deposition energy of Cu clusters affect the final density of thin films grown by cluster deposition. We have also presented a model showing how surface energy, released during cluster impacts, increases film density. Thin-film densities

are lowered as cluster size increases, up to a threshold value in cluster size, of approximately 1000 atoms, after which clusters no longer stick to each other as easily. At the largest cluster sizes, film densities stabilize to their lowest level. A rapid increase in film densities can alternatively be achieved by increasing deposition energies.

These results lead the way toward a more efficient control of the quality of thin films that can be grown by cluster deposition. By varying the size or the deposition energy that is used during deposition, films of a specific density can be achieved. Deposition parameters for both the growth of dense films, as well as the growth of porous, possibly nanostructured thin films can be deduced from these results. Cluster deposition can offer a wide variety of possible outcomes that are within reach only if the correct conditions of growth are known.

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