Contact epitaxy in multiple cluster deposition

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The specific properties of cluster-assembled thin films depend heavily on the size of deposited clusters as well as the energy with which they impact the substrate. When depositing at thermal energies, small enough clusters will align completely epitaxially with a smooth substrate, whereas larger clusters may form structures containing grains. As more clusters are deposited, however, they will no longer impact on a smooth surface, but rather on a surface roughened by previously deposited clusters. Using molecular dynamics simulations, the authors have determined the upper limit in cluster size for epitaxial deposition of multiple copper clusters at temperatures ranging from 0 to 750 K. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2410220]

A comprehensive understanding of cluster-surface interactions is crucial for the development of applications that utilize nanocluster deposition techniques. For example, growth of nanostructured surfaces is severely complicated by effects related solely to the specific sizes of clusters deposited. Experiments have shown that, for instance, metal clusters of small enough sizes will align completely epitaxially with the surface of a smooth substrate, even when deposited at very low energies.[1,2] In a previous study we determined that this is a temperature dependent phenomenon, where the upper size limit for clusters that will exhibit such complete contact epitaxy is roughly linearly dependent on the temperature of the substrate.[3–5]

As deposition continues, however, clusters will no longer necessarily impact on a smooth surface, as the previously deposited clusters cover it with hillocklike protrusions. In order to grow complete films with well tailored properties, it is therefore important to understand how the upper size limit of complete contact epitaxy is affected, if the deposition of clusters occurs on rough surfaces, i.e., when multiple clusters are deposited.

In this work we have simulated the deposition of multiple Cu cluster impacts on an initially smooth (100) Cu surface, thereby mimicking the initial stages of thin film growth. The maximum cluster size, resulting in the growth of an epitaxial structure, was determined for different amounts of deposited clusters in the temperature range of 0–750 K.

Classical molecular dynamics (MD) simulations were used to deposit a sequence of up to eight equisized Cu nanoclusters on a smooth (100) Cu substrate. Cu atom interactions were described with the use of Foiles' embedded-atom method potential.[6] The Berendsen temperature control algorithm[7] with a time constant of 300 fs was used to stabilize the temperature at the borders and the bottom of the simulation cell.

The clusters were given the shape of Wulff polyhedra,[8] with the dimensions of each cluster volume optimized to the configuration of minimum surface energy, as was the case for deposition of single clusters on a smooth surface.[3,4] Other potentials and initial cluster shapes were also tested, for which no significant differences were observed. Each case of cluster size and temperature was repeated up to 20 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 a kinetic energy of 5 meV/at. The clusters were then relaxed for 2 ns before the next clusters were deposited on top of them, at positions chosen randomly with respect to the previously deposited structure. All clusters were rotated to random orientations prior to deposition.

The degree of epitaxy for the deposited cluster structures was analyzed both visually and numerically. Numerical analysis was carried out by calculation of the factor F_{epi}, also used in previous papers.[3,9] F_{epi} gives a measure of the average displacement of atoms in a cluster, as compared to what their positions would be in a perfect continuation of the substrate lattice. Offset in ideal atom positions, due to strain or the existence of seperate grains, will contribute to a raising of F_{epi}. A low value of F_{epi} can therefore be attributed to a high degree of epitaxy.

Visual analysis showed that the interaction between thermally deposited Cu nanoclusters and rough Cu substrate surfaces does not qualitatively differ much from what was previously observed for clusters deposited on smooth (100) Cu substrates.[3,4] Once the cluster approaches sufficiently close to the surface, it accelerates rapidly and impacts with higher kinetic energy than what corresponds to the deposition energy. The initial deformation of the cluster is caused by a local temperature increase in the proximity of the impact, which is a result of this elevated cluster velocity.[10]

Figure 1 shows the average potential energy of the atoms in the first, second, and third Cu_{38} clusters deposited, with coinciding impact points, at 0 K. The rapid drop in potential energy, observed in the fraction of a picosecond before impact, is responsible for the increase in kinetic energy experienced by each cluster; in effect, it is the release of binding energy, related to a lowering of surface energy for both the cluster and the substrate. For all clusters the behavior is somewhat similar, as the average potential energy decreases exponentially in conjunction with the impact, after which the potential energy decreases more slowly as the cluster settles on the surface.

The main difference between clusters impacting on a rough surface, as compared to those impacting on a smooth surface, is the magnitude of the initial lowering in potential energy. Although this initial decrease is thereafter followed

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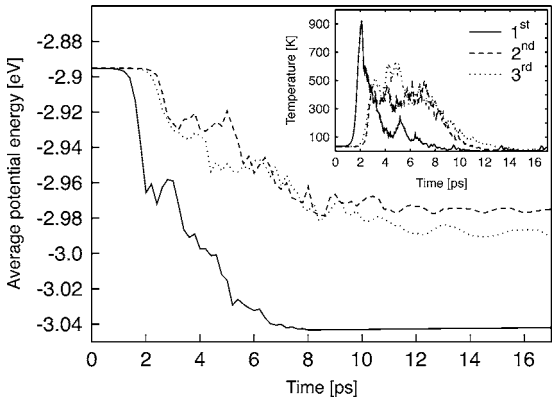

FIG. 1. Average potential energy of the atoms in the first, second, and third Cu_{38} clusters deposited on a smooth substrate at 0 K. The inset shows the local increase in temperature associated with each impact.

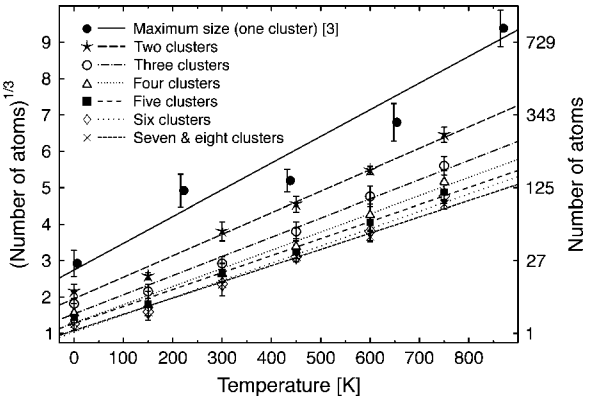

FIG. 3. Maximum size of Cu clusters that achieve full contact epitaxy when multiple amounts of clusters are deposited in sequence on a Cu substrate as a function of the temperature of the substrate.

by a continued lowering of the potential energy, as the cluster settles into its final position, it is mainly this initial lowering that causes an extreme increase in the temperature of the cluster's local surroundings. The inset in Fig. 1 clearly shows how a temperature increase occurs simultaneously with the initial drop in potential energy.

If the first cluster deposited on a smooth surface is close to the upper limit in size for complete contact epitaxy, it will form a hillocklike structure. As a second cluster approaches this structure it will interact with a smaller projected surface area, due to the curvature of the hillock. Figure 2(a) illustrates how the projected surface area of interaction is much larger for the cluster approaching a smooth surface than it is for the cluster approaching a hillock, in Fig. 2(b), even though their interaction range is the same. Figure 2(c) shows a snapshot of a situation, similar to that of Fig. 2(b), occuring in the MD simulations.

The total potential energy of the second cluster may later approach that of the initially deposited cluster, as it further relaxes on the surface, but the increase in local temperature resulting from the initial rapid increase in kinetic energy will be less than for a cluster approaching a smooth surface. In a related paper we show that a cluster will align completely epitaxially due to the increase in kinetic energy occurring at impact, only if the momentary elevation in temperature rises above the superheating melting point of the cluster.[11,12]

Because the surface to volume ratio of clusters, and hence surface energy per atom that is released upon impact, increases as their size decreases, the use of smaller clusters will result in higher local temperatures upon impact. This compensates for lowering caused by the interaction with a rough surface. A previous study has shown that the probability of a single cluster achieving complete contact epitaxy can also be raised, if momentary temperatures are increased through the use of higher deposition energies.[13]

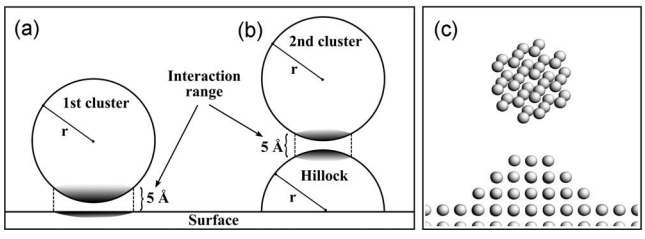

FIG. 2. Schematic diagram, showing the differences in projected surface area of interaction between (a) a cluster and a smooth surface, and (b) a cluster and the hillock remaining after a previous cluster impact. (c) shows a snapshot of a Cu_{38} cluster approaching a hillock.

Visual analysis showed that a lower local temperature during cluster relaxation also results in a more restrained lateral spreading of the cluster, and hence a smaller radius of curvature for the resulting hillock structure, independent of whether the structure is epitaxial or not. As the next cluster approaches this sharper apex, it will experience an even lesser increase in temperature. This sharpening of the apex will continue until the smallest possible radius of curvature is achieved.

The minimum hillock radius is limited by cluster size, and will therefore eventually decrease to approximately the cluster radius. The following clusters deposited will thereafter experience the same average potential drop and, consequently, the same local temperature increase. This can clearly be seen in Fig. 1 for the case of the second and third clusters. As the deposited structure grows in height, dissipation of heat from the impact will, however, slow down, thereby allowing for a longer period of time at elevated temperatures.

The upper size limit of complete contact epitaxy decreases for each additional cluster deposited on an initially smooth surface, as can be seen in Fig. 3. The magnitude of this decrease, however, subsides as the amount of deposited clusters increases, eventually approaching a level where all additionally deposited clusters experience the same local temperature increase upon impact. This effect may allow for the possible growth of thicker epitaxial films using cluster deposition.

The maximum cluster radius (approximately the cube root of the number of atoms it contains), for clusters that reach complete contact epitaxy, is, to a close approximation, linearly dependent on substrate temperature during deposition, for all amounts of clusters deposited.[5] Small enough grains, if still remaining in the cluster after its initial rearrangement, can later be relaxed through grain boundary dislocation reactions, more specifically the untwinning of twin boundaries, caused by thermal motion of Shockley partial dislocations at the grain boundaries.[11,14] These mechanisms will be described in greater detail in a related paper.[11] Relaxation of deposited clusters is a combination of rapid rearrangement due to the initial increase in local temperature and such long term dislocation reactions.

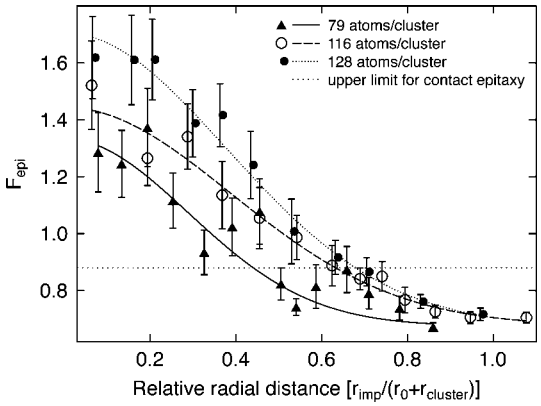

FIG. 4. F_{epi} of the second deposited cluster, when two equisized clusters of sizes 79, 116, and 128 atoms per cluster were deposited in sequence on a 300 K substrate as a function of the normalized radial distance between the impact point of the second cluster and the center of the first. $F_{epi} \approx 0.7$ corresponds to perfect epitaxy, whereas epitaxial configurations with higher values of F_{epi} are strained. The dotted line corresponds to systems determined epitaxial through visual analysis.

Epitaxial growth through deposition of clusters is, however, affected by several other beneficiary factors. The likelihood for epitaxial alignment of each cluster may, for instance, vary significantly depending on the impact point of the cluster with respect to already deposited clusters.[9] Figure 3 depicts the upper size limit of contact epitaxy for deposition at conditions where epitaxial alignment is least likely. Actual deposition may in fact allow for the alignment of larger clusters.

Figure 4 shows the calculated F_{epi}, for different cases of the second deposited clusters, as a function of the radial distance of their impact points from the center of a previously deposited cluster. The radial distances of impact r_{imp} on the x axis are normalized with the sum of the radii of both the first, r_0, and the second cluster, $r_{cluster}$; hence a radial distance of more than 1.0 corresponds to a situation where the two clusters do not touch at the moment of the second cluster's impact on the surface, i.e., the second cluster is *de facto* deposited on a smooth surface.

It can clearly be seen from Fig. 4 that the likelihood of a nonepitaxial configuration increases as the point of impact for the second cluster approaches the center of a previously deposited cluster. The calculated F_{epi} is higher for smaller radial distances due to a greater degree of strain and disorder for those resulting structures.

Lower deposition rates, associated with contemporary cluster sources, will also positively affect the epitaxial alignment of deposited clusters. If allowed to relax at sufficiently high temperatures, epitaxial cluster hillocks will eventually form atomic monolayers through long-time-scale thermally activated surface migration.[15] During actual cluster deposition, time between impacts, given typical fluxes of the order of 10^{12}–10^{15} clusters/(cm^2 s), will on average approach the order of milliseconds, rather than the 2 ns used in our simulations. Cluster hillocks will experience significant flattening at temperatures above 300–500 K, thereby improving conditions for clusters deposited on top of them. At lower temperatures, where thermally activated mechanisms are of less critical importance,[11] the results of this letter are valid for any realistic flux.

In conclusion, we have determined that the upper limit in size of clusters that will achieve complete contact epitaxy is lower for deposition of multiple clusters than for single cluster deposition. This lowering is caused by a lesser increase in local temperatures if clusters are adsorbed on a rough surface. Noncoincident impact points and thermally activated surface migration will, however, favor epitaxial alignment.

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