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Kinetics-limited surface structures at the nanoscale

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This letter presents the evolution of kinetics-limited nanoscale structures during copper thin film deposition. We first calculate the three-dimensional Ehrlich–Schwoebel (3D ES) kinetic barrier of copper using the molecular dynamics/statics method. Based on this calculation, the dimension of {111} facets, under typical sputtering deposition conditions, is estimated to be 700 nm if the 3D ES barrier is effective, in contrast to 70 μm without it. Accompanying the calculations, we deposit copper ⟨111⟩ columns using the magnetron sputtering technique, and characterize their structures using scanning electron microscopy and x-ray diffraction techniques. The observed facets of pure copper films are on the order of 200 nm in dimension, confirming that surface structure is controlled by the 3D ES kinetic barrier. When indium is introduced as surfactant, the facet dimension increases, leading to conformal films; this is attributed to reduction of the 3D ES barrier. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1555278]

Thin films are used in a wide range of engineering applications, such as interconnect metal lines in integrated circuits.[1] The microstructure evolution of thin films during deposition, particularly texture development, dictates their performance. An atomistic simulator has been developed for this purpose.[2,3] It provides a means of simulating texture competition of thin films (of less then 0.1 mm in dimension) at the atomic level and under realistic deposition rates. Further, when linked with large-scale simulators such as FEBEL,[4] it may provide a unique capability of rigorously simulating microstructure evolution of large-scale thin films. Within this framework, details of such physical mechanisms as interface diffusion and grain boundary migration are pivotal in making simulations predictive.

One important aspect of interface diffusion is the migration of an adatom down surface steps. In 1966, Ehrlich and Hudda experimentally observed the effect of surface steps in obstructing adatoms from migrating down the step, indicating the existence of an extra energy barrier to step diffusion.[5] In the same year, Schwoebel and Shipsey proposed a similar concept, citing their own experiment together with the Ehrlich–Hudda experiment.[6] This extra barrier has since been named after them, or sometimes after one of them. Here, we call this quantity Ehrlich–Schwoebel (ES) barrier. It is worth mentioning that the original ES barrier refers to an adatom diffusing down a straight step of a monoatomic layer. In this regard, we call this quantity a two-dimensional (2D) ES barrier, to facilitate the discussions later. In studying epitaxial growth, particularly the 2D–three-dimensional (3D)–2D transition as a function of temperature,[7] the ES barrier at the corner of two intersecting steps has been recognized. This quantity at the corner may be termed a one-dimensional ES barrier for the migration of adatoms between facets. Recently, we have proposed the concept of the 3D ES barrier, calculated its values for aluminum, and discussed the possibility of its impact on surface faceting,[8,9] as reviewed by Lagally and Zhang.[10] Combining molecular dynamics/statics simulations and magnetron sputtering deposition experiments, in the following we present the evolution of nanoscale structures on copper surfaces and correlate them with the 3D ES barrier.

We start with the molecular dynamics/statics calculations of the 3D ES barrier in copper. The simulation method is similar to that in reference,[8] and will be only briefly summarized in the following. The interatomic interactions are described by the embedded atom method.[11] A simulation cell with a flat surface, say {111} or {100}, is first chosen. An island of multiple layers is introduced on top of the flat surface. The island is constructed so that the top surface is parallel to the substrate, and the side surfaces consist of {100} and {111} facets. For a typical simulation cell, one may refer to Fig. 1, except that surfactants are absent in the molecular dynamics/statics simulations. Atoms in the bottom region of the simulation cell are fixed to their perfect lattice positions to mimic a semi-infinite large bulk under the surface. The convergence of numerical results is tested against the size of simulation cell, which is chosen so that the energy calculations are convergent up to ± 0.01 eV. The results are summarized in Table I; note that the ES barriers here refer to the total barriers, not just the extra barriers beyond that on a flat surface. Because of the vast information accumulated on copper surface diffusion, from both experiment and simulation, we will compare our calculations with others in a de-

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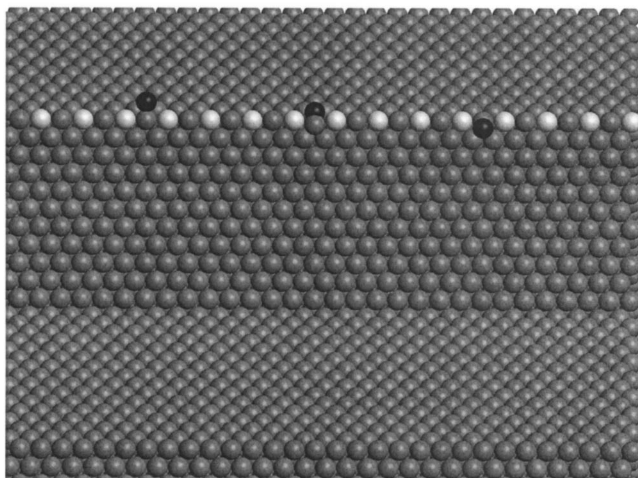

FIG. 1. Configuration of surfactants (lighter gray) at the ridge separating two {111} copper facets. The three dark spheres represent a migrating adatom at three configurations during diffusion, from left to right: initial, saddle point, and final states. The regular copper atoms are represented by medium-gray spheres.

tailed report later. Since faceting generally is the most prominent on {111} surfaces of fcc metals, we have calculated the 2D ES barrier for only this surface. As shown in the Table, even the smallest 3D ES barrier involving {111} (0.33 eV) is substantially larger than the 2D ES barrier of 0.10 eV (or 0.06-eV extra barrier compared to the 0.04-eV on a flat surface), or than the adatom migration energy of less than 0.09 eV.[12,13]

For thin films with ⟨111⟩ facets on top, their dimension may be limited by this large 3D barrier. Take typical physical vapor deposition conditions as 0.07 μm per minute and room temperature; the value 0.07 is chosen for easier comparison with experiments later in this letter. Assuming that adatom diffusion is not much impeded by clustering and that it diffuses during time t when one monolayer is deposited, we can calculate the distance of its diffusion $\sqrt{2Dt}$, where D is the diffusion coefficient of the adatom. This distance gives an estimate of the dimension of flat surfaces (facets). Taking the upper limit of adatom migration energy on the flat {111} surface as 0.09 eV,[12,13] and the attempt frequency 10^{13} per second, we estimate the facet dimension to be 80 μm. If the facet dimension is limited by the 2D ES barrier, it will be about 65 μm. Both of these dimensions are very large: on the order of 70 μm. Now, using the smallest 3D ES barrier involving a {111} facet (0.33 eV) as the activation energy, we estimate the facet dimension to be 700 nm: two orders of magnitude smaller than 70 μm.

TABLE I. Ehrlich–Schwoebel barriers and adatom migration energy on {111} surface of copper; all energies are eV.

3D ES barriers:		
	{111}→{111}	0.33
	{111}→{100}	0.40
	{100}→{111}	0.67
	{100}→{100}	0.20
2D ES barrier on {111} stepped surface:		
	⟨110⟩/{111}	0.10
	⟨110⟩/{100}	0.34
Adatom migration energy on flat {111} surface:		0.04

Note: The first column indicates the starting and final facets for 3D, and step types for 2D ES barriers.

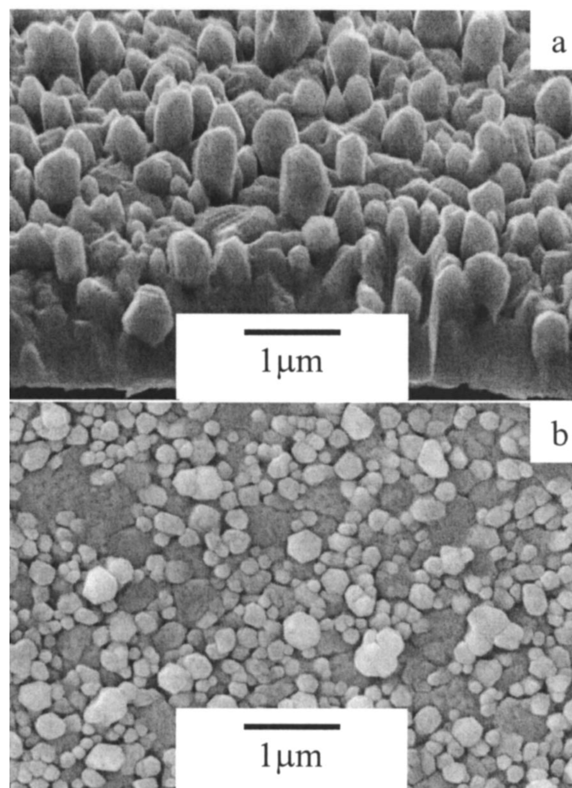

FIG. 2. (a) Cross-sectional, and (b) top-view SEM of pure copper thin film.

Since the 3D barrier limits the facet dimension, its reduction should lead to enlargement of the facet. We here propose a mechanism of reducing the 3D ES barrier by introducing surfactants, as shown in Fig. 1. Take indium as the surfactant, the choice is again for easier comparison with experiments later. Based on the sublimation energies of indium and copper,[14] we estimate the bond strength of indium as 71% that of copper. As a rough estimate, the indium–copper bond strength can be geometrically interpolated as 84% that of copper–copper. As a result, the 3D ES barrier should also be reduced to 84% of the 0.33 eV; that is, 0.28 eV. As a result, the corresponding facet dimension should be tripled.

To experimentally verify the dominant role of the 3D ES barrier in facet dimension, we deposit faceted copper columns using the magnetron sputtering technique. The experimental setup and procedures are similar to that in Ref. 15, and will be briefly outlined here. The sputtering power is fixed at 100 W, and the chamber is filled with 99.999% Ar, flowing into the chamber at a rate of 9 sccm. During the deposition, the base pressure is kept at about 6.7×10^{-6} Pa (or 5.0×10^{-8} Torr) and the working pressure at about 0.4 Pa (or 3.0×10^{-3} Torr). The target is a block of 99.995% copper, and the substrate is about 4 cm away and kept at room temperature (22% of the melting temperature). We estimate the deposition rate, from the film thickness, to be about 0.07 μm/min. The faceted pure copper film, 1-μm thick, is characterized by scanning electron microscopy (SEM), and its cross sectional and top views are shown in Figs. 2(a) and 2(b). All films are kept in the vacuum chamber for about 2 h

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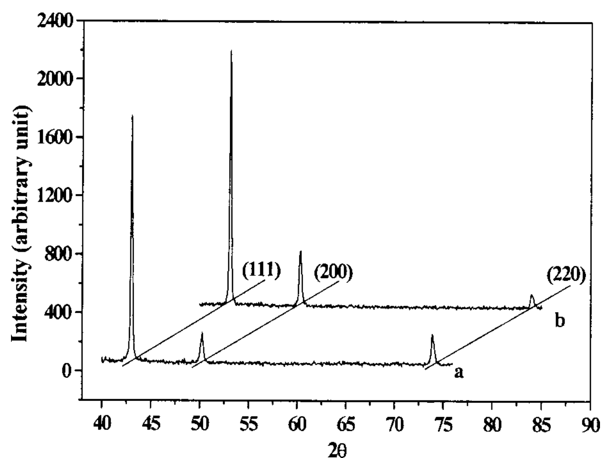

FIG. 3. XRD of the pure and the indium-mediated copper thin films. Curve *a* corresponds to the pure copper thin film, and *b* the indium-mediated copper thin film, as shown in Fig. 4.

at room temperature before the SEM pictures are taken. Figure 2(a) shows that the columns are covered with faceted surfaces. Figure 2(b) further shows that the border of columns is usually hexagonal, consistent with the faceting simulations.[2] As shown by the x-ray diffraction (XRD) characterization in Fig. 3, the film is of $\langle 111 \rangle$ texture; the top surfaces are therefore of $\{111\}$. The dimension of these facets is measured to be about 200 nm from the SEM picture, confirming that the 3D ES barrier controls the facet dimension, in contrast to 70 μm if the 3D ES barrier has no effect. Next, we introduce indium as surfactant during deposition. A layer of indium of $\sim$1 nm in thickness is deposited when the pure copper film is 0.5-μm thick. The copper deposition is temporarily suspended when indium is deposited, and then continued until the copper film is 1-μm thick. The deposited indium is more than one monolayer thick, so as to have enough indium atoms floating on the film surface even if some of them are buried by subsequent deposition of another 0.5 μm of copper. The indium-mediated copper thin film is characterized by SEM, and its cross section is shown in Fig. 4. The film is uniform, indicating that the facet dimension has been increased. The spacing of faceted columns in Fig. 2 is no larger than three times the facet size. If the facet size is increased by a factor of three, the columns will meet each other to form uniform films. This uniformity is indeed the case, as shown in Fig. 4, supporting the proposed mechanism of 3D ES barrier reduction in Fig. 1. Incidentally, the indium-mediated copper film is also more strongly $\langle 111 \rangle$ textured, as shown in Fig. 3; this feature may be beneficial to interconnect metallization processes.

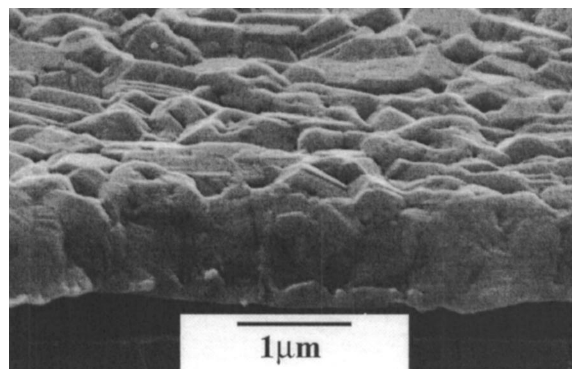

FIG. 4. Cross-sectional SEM of indium-mediated copper thin film.

In summary, we have presented the evolution of nanoscale structures on surfaces of copper thin films. The structure (facet) dimension is shown to be controlled by the 3D ES barrier, and can be increased by the introduction of indium as surfactant. These results also provide indirect evidences on the existence of the 3D ES barrier, and the feasibility of its modification through surfactants.

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