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Atomistic Monte Carlo simulations of three-dimensional polycrystalline thin films

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An atomistic Monte Carlo code to simulate the deposition and annealing of three-dimensional polycrystalline thin films is presented. Atoms impinge on the substrate with selected angular distributions, and grains are nucleated with different crystalline orientations, defined by the tilt and rotation angles. Grain boundaries appear naturally when the islands coalesce, and can migrate during both deposition and annealing simulations. In this work we present simulations of aluminum films. We examine the influence of the temperature, deposition rate, and adhesion to the substrate on the morphology of polycrystalline thin films. The simulations provide insight into the dominant microscopic mechanisms that drive the structure evolution during thin film processing. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1577814]

I. INTRODUCTION

The deposition of polycrystalline thin films is essential to the fabrication of microelectronic devices. About half of the processing steps are devoted to deposition of metal conductors, diffusion barriers, and insulator films during the metallization phase of manufacturing. The performance and speed of ultralarge scale integration (ULSI) devices is driven by their ever decreasing feature sizes, which have been shrinking exponentially according to Moore's law. In this scenario, the microstructure and properties of conducting thin films are a crucial issue for reliable interconnection circuits.

Considerable work has been done in recent years, both experimental and theoretically,[1–4] to characterize and predict the properties of thin films from external conditions, including the temperature, deposition rate, type of substrate, deposition process, angular distribution of atoms, and incident kinetic energy. A number of simulators have been presented in the literature to deal with the different aspects of thin film deposition.[5–10] Several solutions have been proposed to overcome the difficulty of handling sites belonging to different crystalline orientations within the same simulation system. A solution proposed in a three-dimensional (3D) Monte Carlo atomistic approach is to use a unique orientation but assign labels to different regions, associating different labels with different crystalline orientations.[5,6,9] Atoms in the middle of two regions are assigned to the grain boundaries. Bruschi *et al.*[7,8] used an atomistic Monte Carlo scheme that represents polycrystalline films in two dimensions. Other authors,[10] instead of using a fully atomistic approach, employed a fundamental unit consisting of cubic blocks containing about 1000 atoms. Each block is assigned an orientation when it is incorporated into the film.

We have developed a full 3D Monte Carlo atomistic code to help understand the role of the elementary atomistic diffusion mechanisms on the deposition and thermal processing of polycrystalline thin films.[11,12] In the work presented here the code has been applied to simulate aluminum deposition and annealing under different experimental conditions, i.e., temperatures, deposition rates, and substrate types. The grain size and morphology of the film resulting from the different conditions are analyzed.

II. COMPUTER MODEL

In order to present our computational model we will first introduce the framework in which atoms are to be placed and then we will present some concepts on the time evolution of the simulation and the events that can take place.

A. Simulation cell

The simulation cell is divided into a grid of 3D boxes (Fig. 1). A box is a portion of space that can contain sites to accommodate atoms, and belong to one or more crystal orientations. In this work, we consider the face-centered-cubic (fcc) lattice of aluminum. A crystal orientation is specified by its tilt and rotation angles. At the beginning of the simulation, all of the boxes are empty (no lattice sites), and therefore inactive. When an atom arrives at the substrate/film, it must be placed on a lattice site. If around the point of arrival there are no sites defined yet, the box containing that point is filled with empty lattice sites belonging to an arbitrary crystal orientation, and the atom is placed on the nearest site. The selection of this orientation can be done either randomly or according to some rules that represent the substrate structure. Afterwards, more crystal orientations can be added to that box, and the atoms will be able to occupy sites that belong to any of them. If an atom from a specific crystal orientation moves within a box and it reaches the border with an inactive

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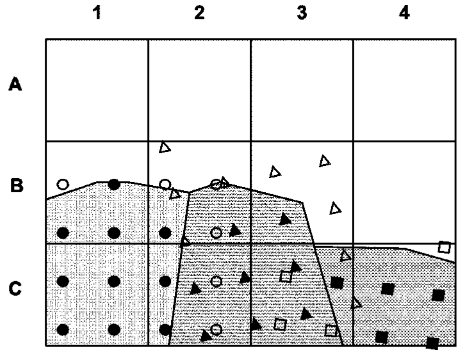


FIG. 1. Example of a simulation cell with 12 boxes, 5 inactive and therefore void of sites (A1–A4 and B4), and 7 active. A closed symbol corresponds to a lattice site that is occupied by an atom, and an open symbol to an empty site. The polycrystalline film has three grains that belong to different crystal orientations. Box C1 is a bulk box inside a grain, and it has sites from just one orientation. Boxes B2, B3 and C3 contain grain boundaries, and therefore sites in them belong to at least two crystal orientations.

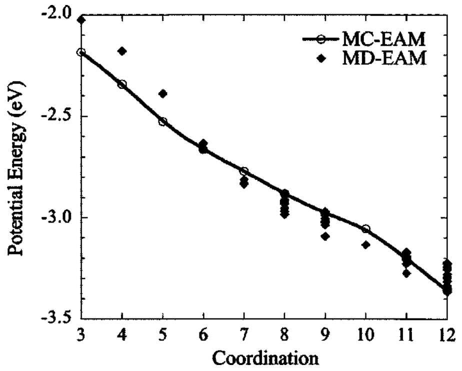


FIG. 2. Potential energies of aluminum atoms plotted as a function of the coordination number (see Ref. 5).

box, a lattice extension with the same orientation is created in the inactive box, making it active. In this way, as can be seen in Fig. 1, the minimum number of boxes that encompass the polycrystalline film are activated, thus conserving memory resources in the computer.

In the case of a polycrystalline film, a box that contains grain boundaries will have atoms and sites belonging to more than one orientation, whereas a box completely inside a grain will be filled with atoms from just one orientation. A box where all the sites are occupied by atoms belonging to just one orientation can be reconstructed very easily, so this allows the removal of most of the information about the box from memory, to further conserve space.

Sites inside a box have an array of pointers to their nearest neighbor sites, either in the same box or in adjacent ones. In case there are also neighboring sites belonging to different orientations, additional pointers are added so that the site is aware of all neighboring ones that are possible targets for a jump in diffusion. Once inserted, sites of a given orientation are never removed from a box, even if the orientation has no atoms occupying its sites as a result of grain boundary migration. So, to speed up the simulation, all of the look-up operations are performed just once, during site creation, instead of looking for neighbors after each event. Once the sites are created, they can be occupied by atoms. Each site has a pointer to a data structure, with information on the identity of the occupant, if there is one, and on the coordination number that an atom would have if present.

As for the box size, if the boxes are too small, the film profile and grain boundary evolution make it necessary to create new boxes almost continuously to accommodate atoms. In this case, practically all the sites in these boxes will be occupied, saving memory resources but reducing efficiency in computation time. On the contrary, because the film evolution is difficult to predict, if the boxes are big maybe an important fraction of their sites will not be used afterwards. However, the box creation process is necessary only from time to time and the procedure is less time consuming if boxes are big. In the simulations presented here, cubic boxes with six lattice units on each side have been used. On the other hand, the total number of orientations that can be created during a simulation will depend on the memory of the computer.

B. Deposition and diffusion mechanisms

The timing of the simulation is controlled by an event manager, which contains a list of all possible events in the system, classified according to their rate. For the simulations of aluminum, only two types of events have been included in the code. First, there are events with periodic occurrence, like the deposition of a new atom from the vapor, which depend on the deposition rate. The other process currently implemented is diffusion, which is modeled as jumps of atoms to neighboring sites. Each atom has a list of possible jumps. This list is updated just after each event in the system if the current atom or site is involved in it.

When a jump is performed, the simulation time is incremented in $\Delta t = 1/\Sigma n_i \cdot \nu_i$, where n_i is the number of jumps of class n and ν_i their rate. The event manager chooses an event with a probability that is proportional to its rate. The rates of each diffusion event are calculated using

$$\nu_i = \nu_{0i} \exp-[(E_{\mathrm{mig}} + \Delta E)/kT],$$

where E_{mig} is the migration energy that depends on the coordination. $\Delta E = E_{\mathrm{final}} - E_{\mathrm{init}}$ is the difference between the energy of the system after and before the jump, if that difference is positive, and $\Delta E = 0$ if it is negative. In our case, as a quick and simple way of calculating this difference, we assume that E_{final} and E_{init} just depend on coordination of the jumping atom, defined as the number of its first neighbors. In Fig. 2 the potential energy of an aluminum atom as a function of its coordination is shown.[5] Only coordination numbers of 3 or greater are included, since atoms on lower coordinated sites are unstable and move to another site. The distances and angles between atom sites inside a grain having the same crystalline orientation are assumed to be those of a perfect fcc crystal. In this way, the rates given by the above equation can be tabulated for the different jumping possibilities, thereby reducing computation time during the simulation and making the code more efficient. However, a question arises for sites near a grain boundary. In the simulations presented in this article we chose a simple approach for calculating the energy of a site near a grain boundary: the coordination is the number of first neighbors in the same grain and the energy is purely determined by this coordination. Atoms with no empty neighboring sites are not able to contribute to mass transport, since an exchange with a neighbor does not produce a net displacement of material. Such atoms are therefore not included in the lists maintained by the event manager. The active particles are limited to atoms in or near the surfaces, interfaces and grain boundaries.

In practice, we start with a flat surface whose behavior can be modeled as monocrystalline, polycrystalline or amorphous. Atoms on the substrate are treated as a separate species from the film, so as to have the capability to model the effects of a foreign substrate on adhesion and surface diffusion. Initially a deposition rate is established, which means that periodically a new atom is added to the simulation. In our model, an atom to be deposited is placed at a randomly selected point in a two-dimensional plane that represents the sputter target. It is then launched towards the substrate at normal incidence, corresponding to perfect collimation of the sputtered flux. Other angular distributions for incident particles, such as the cosine to represent the sputter deposition, can be readily implemented.

When an atom hits a bare substrate, a new box with empty sites is created to accommodate the atom. The new lattice tilt and rotation angles are chosen either randomly or based on the substrate properties. If the substrate is monocrystalline, the growing film orientation is that of the substrate. If the substrate is polycrystalline, regions on the substrate can be defined for the orientation of new islands to be an extension of the corresponding substrate regions. The atom then starts jumping from site to site on the substrate. As stated above, possible target sites are only those with coordination number of 3 or greater. The substrate below an atom or atoms belonging to a specific orientation is assumed to be formed by occupied sites with the same orientation. The difference with the bulk is that the adhesion energy of an atom to a substrate atom is a parameter that can be varied. Lattice mismatch effects between the substrate and the film are not taken into account.

If, during deposition, an atom enters an active box containing empty sites, the atom travels through it until it finds some stable site, one with a coordination of 3 or more. If there are several stable sites close to that one, the atom is placed on one of them, which is selected randomly. No evaporation of atoms was allowed in the simulations presented here. Between deposition events, surface or interface diffusion can take place.

It is important to model the grain boundary dynamics in a realistic, but simplified way. In our model, atoms near boundaries were allowed to jump to neighboring sites, possibly changing membership from one grain to another. Relaxation at grain boundaries is not taken into account. Near a grain boundary (Fig. 3) we consider that there are several possible target sites (A2, B1) for a jumping atom at site A1, each belonging to a different crystal orientation. The rate for this process corresponds to the jump from A1 to A2, both in the same grain. When the atom is going to jump, it checks the energy of the nearest site (B1) in the adjacent microcrystal. If the atom coordination at A2 site is lower than that at the B1 site and, correspondingly, the atom has a lower energy at B1 than at A2, it will move to B1. Otherwise it remains at the A2 site. This atom exchange mechanism is allowed if the A2 and the B1 sites are close enough. In our simulations we have set this maximum distance to 0.7 times the nearest neighbor distance. Evaluation of the distance is performed just once, when the sites are created. With this relatively simple, energy-driven atom exchange mechanism, grain boundary movement emerges as a ‘‘macroscopic’’ result of the atomistic mechanisms.

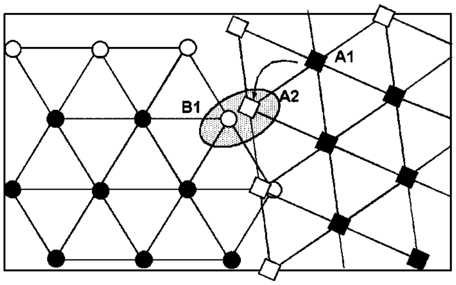


FIG. 3. Mechanism for grain boundary movement due to jumps to adjacent target sites that belong to different crystal orientations. Jumping atom A1 will choose empty site B1 (on an adjacent grain) to minimize energy (higher coordination than empty site A2).

III. RESULTS OF POLYCRYSTALLINE THIN FILM DEPOSITION

To test the code described above, we have studied the influence of the temperature, deposition rate and substrate conditions on the microstructure of thin films. First we carried out a simulation of the growth and annealing of a film at a given temperature and deposition rate, and then two more simulations with all but one of the parameters unchanged; in one case a higher temperature is simulated, and in the other a lower deposition rate. All of these simulations were on a polycrystalline substrate. Other simulations have been carried out to examine the influence of the substrate on the microstructure. Here we compare different values of the adhesion of the film to the substrate, assuming it is amorphous. Overall, these simulations prove that the 3D models implemented, although simple, are capable of capturing the dominant mechanisms involved in polycrystalline metal deposition and annealing.

In the simulations, surface diffusion was reduced by using a migration energy barrier of 0.60 eV for all surface sites. This value is larger than those obtained either from molecular dynamics (MD) simulations or first principles methods for atoms with low coordination numbers, i.e., the atoms with the highest mobilities.[5,13] Therefore a simulation at a given temperature would correspond roughly to an experiment performed at a lower temperature.

A. Polycrystalline substrates: Influence of temperature and deposition rate

First we simulated the growth of an aluminum film on polycrystalline aluminum at 80 °C and its subsequent annealing at 300 °C for 0.3 s. Atoms were deposited at a rate of 0.25 μm/min. The total number of atoms deposited was

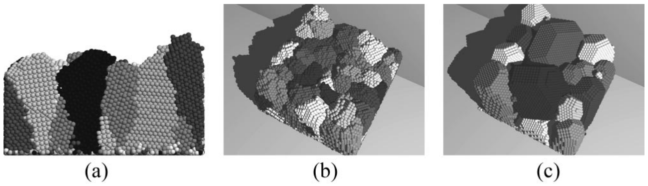

(a) (b) (c)

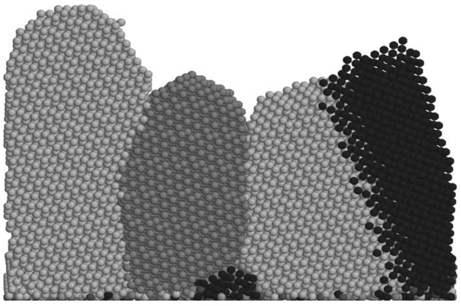
FIG. 4. Cross section (a) and perspective view (b) of the sample deposited at 80 °C and 0.25 μm/min just after finishing deposition, and perspective view after annealing (c).

50 000 and the substrate was a square of 120 Å. Ten different crystal orientations, with the angles picked at random, were allowed. As described above, when an isolated atom hits the bare substrate, a new crystal orientation is selected and built with empty sites, with one site at the current location of the atom. When this atom starts to diffuse, jumping between sites from this orientation, it can either find another atom and bind together and form a small island, or find the edge of a step and get attached to it, where it remains for a relatively long time because of the lower potential energy. The cross section and a perspective view of the sample as grown, along with a perspective view of the sample after annealing can be seen in Fig. 4.

Looking at the final sample structure just after deposition, only very small (111) and (100) faces have developed. This is because under these conditions external grain surfaces are mostly rough, due to the small mobility of atoms on the terraces. On the other hand, we have observed that during deposition little grain boundary migration takes place at this temperature. Rather, it seems that grain growth is accomplished by preferential incorporation of atoms at grains with different orientations when they arrive at the top surface. This structure, which shows V-shaped grains [Fig. 4(a)], would correspond to zone T in the structure zone model.[3,14]

After deposition, the sample was annealed at 300 °C for 0.3 s [Fig. 4(c)]. We observe that at this temperature grain boundaries are mobile. Consequently, during annealing, the film microstructure evolves towards bigger grains that grow at the expense of others, until finally only a small number of big grains survive. During the first steps of annealing, faceting appears. Flat (111) facets clearly developed at the top surface, along with some (100) terminations to avoid sharp vertices.

To analyze the influence of the deposition temperature on the film microstructure, we carried out simulations at a higher temperature, 200 °C (Fig. 5). The higher adatom mobility on the substrate gives rise to bigger grains from the beginning of deposition. After nucleation and the first stages of growth, faceting appears, mainly (111) oriented. New adatoms landing on the facets wander around until they find a step, so incorporation of atoms to grains is mainly through terrace growth (ledge displacement). This is in contrast with the 80 °C deposition. In that case, smaller diffusion coefficients resulted in rougher terminating surfaces. To monitor the evolution of the grain structure during deposition at 200 °C, we show a cross section of the sample cut at 17.87 Å at different times (Fig. 6). Grain boundaries are seen to move inside the film during deposition, so grain growth is accomplished by this mechanism, as expected at high temperatures.[2,4] This structure is similar to zone II in the structure zone model.[3,14]


(a)

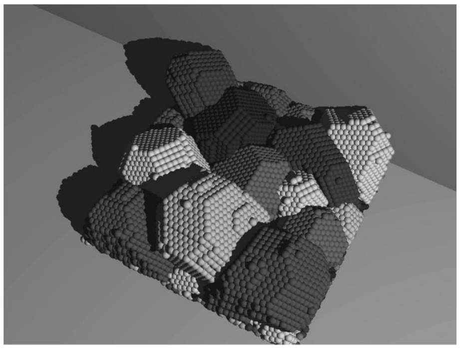

(b)

FIG. 5. Sample deposited at 200 °C and 0.25 μm/min: perspective view (a) and cross section (b). Total deposition time was 1.3 s.

The other important input parameter that determines the structure is the deposition rate. To analyze its effect, we carried out a simulation at 80 °C (same as for the first sample) but using a deposition rate four times smaller, i.e., 0.0625 μm/min. The mobility of the atoms is then the same, but reducing the deposition rate allows the atoms to diffuse for a longer time and thus find, to some extent, more stable sites. As expected, the final microstructure has bigger grains on average with broader terraces on them.

B. Amorphous substrates: Influence of substrate adhesion

Finally, the role of substrate adhesion in the resultant microstructure is analyzed. Two simulations were carried out at 25 °C on an amorphous substrate, each with different substrate adhesion energy. To model an amorphous substrate, all

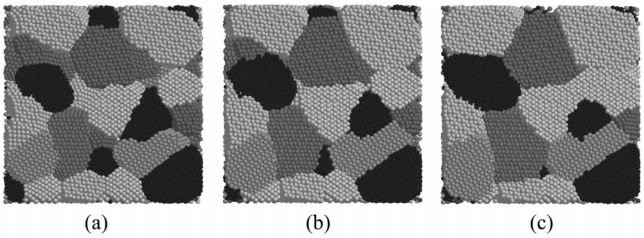

(a) (b) (c)

FIG. 6. Time sequence of plan views at constant height (17,9 Å) showing some grain boundary motion during deposition at 200 °C: 0.5 (a) and 0.79 s (b) and at the end of the deposition, 1.3 s (d).

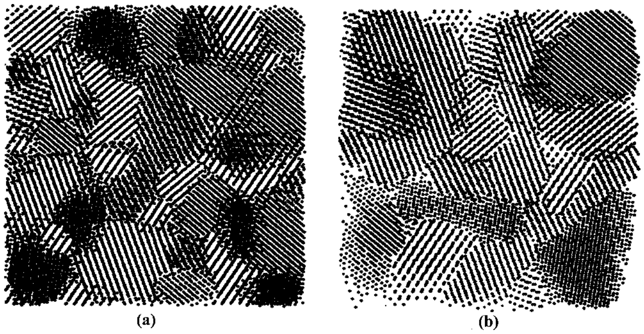


FIG. 7. Top view of samples deposited onto amorphous wetting (a) and nonwetting (b) substrates.

the substrate sites are assumed to be equivalent, i.e., they have the same binding energy to the substrate on average. This is a rough approximation to the fact that the variation in site binding energy on an amorphous substrate is smaller than on a surface containing steps.

Depending on the substrate adhesion, we can have wetting or nonwetting substrates. For the two simulations presented here, the binding energies to the substrate are 3.8 and 1.0 eV, for wetting and nonwetting behavior, respectively. Figure 7 shows a plan view of the final microstructure of the two samples to visualize the different grain size that they exhibit. Figures 7(a) and 7(b) are plan views of the final microstructure for the wetting and nonwetting substrates, respectively. As expected, the weaker the bonding to the substrate, the bigger the grain size and the smaller the number of grains in the film. This behavior is related to the first steps of deposition. When the binding energy to the substrate is low, adatoms are very mobile. In this case, small unstable clusters are observed to form and dissolve very quickly at the beginning of the simulation, but just a small number of them succeed in reaching the critical size, and these give rise to the growth islands, far from each other. Due to the high adatom diffusion, the growth of the existing islands once the critical size is achieved is more probable than the nucleation of new ones. Besides, in this case it has been observed that piling up of atoms is preferred to growing in extension, because it contributes to minimization of the island energy. So when the film thickens, it has a small density of grains. Conversely, if the binding energy of adatoms to the substrate is high, a large number of small stable islands are observed to nucleate very early in the simulation. In this case the critical island size is small. Due to the high density of islands coalescence is soon achieved, resulting in a much smoother film surface than in the previous case. As a result, subsequent atom deposition results in lower grain size than in the nonwetting substrate, and therefore higher grain density.

IV. CONCLUSIONS

An atomistic kinetic Monte Carlo model for simulating deposition and annealing of three-dimensional polycrystalline films was presented. It allows simulation of the evolution of the grain microstructure during nucleation and growth depending on the experimental conditions, such as the temperature, deposition rate and substrate properties.

In this work, within the grains that form the polycrystalline structure, the distances and angles between atoms are the same as those of an aluminum fcc lattice. Different grains have different crystalline orientations, defined by their tilt and rotation angles. Grain boundaries appear naturally at the borders. In order to minimize the computer memory required, the whole simulation cell is divided into regions called boxes that can contain sites from one or more orientations.

Two kinds of events can occur, deposition of new atoms from the vapor and atom diffusion. Deposition is modeled as atoms impinging on the substrate with selected angular distributions with frequency defined by the deposition rate. Atom diffusion is simulated by the jumping of atoms to empty neighboring sites that belong to the same crystalline orientation. Jumps are performed with a probability proportional to its rate, which depends on the migration energy and the difference in system energy after and before the jump. Site energies are assumed to depend on its coordination, i.e., the number of first neighbors.

Near a grain boundary, the target site for a jump may be close to another empty site belonging to a different orientation. In this case the atom will jump to the lower energy site. If the target site orientation is different from the initial one, the jump will contribute to grain boundary motion.

We have tested the models by studying the influence of the temperature, deposition rate and adhesion energy to the substrate on the film microstructure. The simulations show that the higher the deposition temperature, the bigger the grains in the film. Also, it has been shown that grain boundary migration is important at high temperatures.

Simulations with different adhesion energies to the substrate were carried out to model the influence of wetting and nonwetting substrates on the film microstructure. Weaker bonding allows more atom diffusion on the substrate to occur, which leads to a reduction of the number of nucleation sites. This behavior corresponds to a nonwetting substrate. It gives a lower density of grains and, correspondingly, larger grain sizes than the wetting substrate.

In conclusion, we have presented a 3D approach to modeling polycrystal deposition and annealing that, although simple, captures many of the dominant mechanisms and features of grain boundaries.

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