Atomistic simulation of hillock growth

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Abstract

This paper explores the mechanisms of hillock and whisker growth in stressed polycrystalline films by molecular dynamics simulations. The initial geometry consists of three grains with a triple line aligned perpendicular to a free surface, plus a fourth pyramidal-shaped grain implanted between the triple line and the surface. This simulated grain geometry corresponds to that observed in experiments during hillock and whisker growth, with the fourth grain serving as a seed for hillock growth. The simulations, performed under an applied in-plane biaxial compression, reveal an upward motion and growth of the seed grain. The growth occurs by stress-driven grain boundary diffusion from below the seed grain onto some of its internal faces. Accretion of atoms to those faces pushes the seed grain upwards and sideways. The different diffusion and accretion rates at different boundaries also give rise to internal stresses, which can be partially accommodated by grain boundary motion coupled to shear deformation. The hillock growth is countered by surface diffusion, which can slow the growth or even suppress it completely. Other mechanisms involved in hillock growth are also discussed.

1. Introduction

In stressed solids, surface shape changes can be driven by grain boundary (GB) diffusion and can result in the growth of hillocks and whiskers. Examples include hillock growth from thin polycrystalline films due to stresses generated by differential thermal contraction between the film and the substrate [1–3]; hillock and whisker formation in Cu conductor lines due to stresses generated by electromigration [4], and hillock and whisker growth in electrodeposited Sn on Cu due to stresses generated by intermetallic formation [5–9]. Whiskers of this type have been called “proper whiskers” as material is added at the base, in contrast to other whiskers where material from the vapor phase is added at the tip.

Hillock growth and the related phenomenon of whisker growth can be thought of as localized Coble creep. In Coble creep grains can change shape as stresses relax by GB diffusion. The GB diffusion is driven by chemical potential gradients on and between GBs. Such gradients arise from differences between the normal stress components acting on the GBs due to their differing orientations with respect to the stress field. The dependence of the chemical potentials of atoms/vacancies on the GBs due to the normal stress was first proposed by Herring [10]. Near a free surface, such fluxes can lead to upheavals and other surface shape changes. During hillock and/or whisker growth, it is poorly understood why the atoms accumulate at sites that are relatively sparse compared to the grain size.

Avoiding the growth of Sn whiskers, which cause shorts in fine-pitch electronic packages, has recently taken on increased importance because of the Pb-free movement in electronic packaging. For several decades, the addition of 3% Pb to Sn electrodeposits on Cu-based leads has provided an effective method to eliminate whisker growth [11]. Without the Pb addition, Sn electrodeposits form with a columnar grain structure that promotes hillock and whisker growth. The former is more common when the column-
GBs are mobile and the latter when they are immobile [9]. Fig. 1 shows cross-sections and top views of a small and a large hillock in a pure Sn electrodeposit. These hillocks are usually single grains and their growth clearly involves lateral broadening by GB migration below the surface concurrent with the accumulation of material on the surface. The localized diffusive flow is thus spread over a larger surface area, never forming a filamentary whisker.

Only certain grains or locations are selected for the hillock and/or whisker growth. In Sn electrodeposits, typical whisker/hillock number densities are $10^4 \text{ mm}^{-2}$ in material with $10^6 \text{ grains mm}^{-2}$. It has been proposed [9] that occasional wedge-shaped grains may be present at the surface of a deposit. These wedge grains form as part of the normal nucleation of new grains and pinch-off of existing grains during the competitive growth of the (mostly) columnar structure. If the early stage of new grain formation is interrupted by the cessation of plating, a wedge-shaped surface grain would remain. If an in-plane biaxial compressive stress were present, a wedge-shaped grain provides a set of GBs with lower normal stresses than for the majority of GBs in the columnar grain structure. This difference in normal stresses drives a diffusion flux from the columnar GBs toward the wedge GBs. The accumulation of material on these GBs is thought to push the wedge grain above the surface.

In this paper we present molecular dynamics simulations aimed at understanding the atomic mechanisms by which hillocks and whiskers may grow. The simulated geometry consists of a tricrystal with a fourth wedge-shaped surface grain, under an applied compressive biaxial stress parallel to the surface. The early stage of hillock growth is observed at high homologous temperatures when the boundary diffusion flux exceeds the lateral fluxes due to surface diffusion. This study reveals a set of mechanisms that are involved in and can influence the hillock and whisker growth under applied stresses.

2. Methodology of atomistic simulations

Because we were unable to locate a sufficiently accurate interatomic potential for Sn, we chose copper as a model material for which an accurate embedded-atom potential is available [12]. This potential can be downloaded from the NIST Interatomic Potentials Repository at http://www.ctcms.nist.gov/potentials. It was used in recent studies of lattice and grain boundary diffusion and has demonstrated good agreement with experiment [13–15]. The potential is accurately fit to a large database of experimental and first-principles data and reproduces a wide range of Cu properties. The bulk melting point of Cu predicted by this potential is $T_m = 1327 \text{ K}$ (the experimental value is 1357 K). The molecular dynamics (MD) simulations performed in this work employed the ITAP Molecular Dynamics (MD) code [16,17], with an integration time step of 2 fs. The NVT ensemble was implemented, in which the temperature and volume (except as specified by the radial strain rate below) of the simulated system were fixed. Temperature was controlled by a Nose–Hoover thermostat. Hillocks and whiskers of Sn grow at room temperature ($0.6T_m$). However, we performed simulations at a higher homologous temperature, $0.83T_m$ (1100 K), to accelerate the hillock growth and make it readily observable on the timescale accessible by the MD method.

Fig. 1. Sections and top view of large and small hillocks observed on pure Sn columnar grain electrodeposits. Sections were prepared by focused ion beam milling. The hillocks are single-crystalline grains.
The construction of the simulation block for the hillock evolution required special efforts. Because this involved a complex multistep procedure, it will be described below in detail.

Our goal was to create the simplest possible grain structure that would mimic the situation shown in Fig. 1. The following procedure was devised to this end (Fig. 2). First, a symmetrical tilt GB with a [001] tilt axis was created in a rectangular simulation block using standard geometric constructions [13–15]. The grains separated by this GB will be labeled 1 and 2. They terminate at a free surface normal to the tilt axis. A third rectangular grain (labeled 3) with edges parallel to [001], [110] and [110] was then placed on top of this surface. Thus, the [110] direction of grain 3 was parallel to the common [001] direction of grains 1 and 2. Note that the three grains form a non-equilibrium triple junction (TJ) normal to the page (Fig. 2a).

For brevity, all GBs appearing in this paper will be designated by two numbers corresponding to the labels of the adjacent grains (e.g. GB 1–3 between grains 1 and 3), while TJs will be referred to by three numbers (e.g. TJ 1–2–3 between grains 1, 2 and 3).

Next, atoms within 10 Å of the surface, shown in Fig. 2a in gray, were made fixed in their perfect-lattice positions, whereas all other atoms were allowed to move during the subsequent MD simulations. A periodic boundary condition was imposed in the TJ direction, which we will henceforth call direction \( z \). This structure was equilibrated during a 2 ns MD run at 1100 K. During this “annealing” step, the 1–2–3 TJ quickly moved down and reached an equilibrium configuration (Fig. 2b). Although the planes of the 1–3 and 2–3 GBs changed, the crystallographic misorientations of the three grains remained the same. After equilibration, the movements of the GBs and the TJ were limited to small thermal fluctuations. Note that the \( \Sigma 5 \) GB (1–2) is pinned by the fixed region, whereas the other two GBs are pinned by surface grooves.

At the next step, a cylindrical region whose axis coincided with the TJ line was cut out of the simulation block as shown in Fig. 2c. Atoms within a 10 Å thick cylindrical shell at the surface were made partially fixed (restricted). Specifically, these atoms were allowed to move in the \( z \) direction during the MD simulations but not in radial directions (except as specified by the radial strain rate below). Furthermore, the periodic boundary condition in the \( z \) direction was now removed and atoms within a 10 Å thick bottom layer of the cylinder were completely fixed by prohibiting their motion in any direction during MD simulations. With these new boundary conditions, the inner cylindrical region of the simulation block consisting of movable (dynamic) atoms was surrounded by either completely or partially fixed atoms, except at the free surface (Fig. 2c). This structure was then “annealed” by a 2 ns MD run at 1100 K.

Finally, a fourth grain was placed on top of the free surface by aligning its [111] direction parallel to the TJ line (see Fig. 2d where the cylinder has been rotated by approximately 90° and the \( z \) axis is now vertical). The role of the fourth grain was to serve as a seed of a growing hillock. This four-grain structure was “annealed” by running MD for 5 ns at 1100 K. During this equilibration process, three more GBs formed between grain 4 and the three previous grains, along with three more TJs. In addition, grain 4 was found to spontaneously rotate as a rigid body during the first 2 ns of the “anneal”, but the rotation practically stopped by the end of the “anneal”. As a result, the [111] crystallographic direction of grain 4 was misaligned relative to the 1–2–3 TJ line. The fourth grain penetrated into the tricrystal along the 1–2–3 TJ line. The four grains meet at one point 1–2–3–4. This block, containing approximately 323,000 atoms, was used as the initial configuration for the subsequent MD simulations.

Fig. 3 shows the actual snapshots of the simulation block at different stages of its construction. The atoms are colored by the common-neighbor analysis (CNA) using the AtomEye visualization program [18], with yellow regions decorating the GBs and TJs. Fig. 3d and e compare the configurations before and after the spontaneous rotation of grain 4. Fig. 3f shows a cut through all four grains present in the simulation block. The plane of the cut is perpendicular to the 1–2–3 TJ and located just below the surface.

Prior to the MD simulations, the simulation block was uniformly expanded by the thermal expansion factor at 1100 K to minimize thermal stresses. The thermal expansion factor was known from previous calculations [12].

To model the hillock growth, the initial structure shown in Figs. 2d and 3e was biaxially compressed at a constant
strain rate during a 30 ns MD run at 1100 K. To impose a constant strain rate, the lateral dimensions of the simulation block (parallel to the free surface) were scaled uniformly down by a factor of 0.99998 every 10 ps. This scaling was applied to positions of all atoms including dynamic, fixed and partially fixed. After each increment of scaling, the MD simulation continued at the new constant volume (NVT ensemble). Due to the restrictions imposed on motion of atoms within the cylindrical shell, their lateral coordinates $x$ and $y$ remained fixed between the strain increments while the axial coordinate $z$ could vary. At the same time, the dynamic atoms could move in all directions in response to the stresses created by the strain. During the elastic part of the loading, a Poisson expansion occurred in the $z$ direction in response to the lateral compression. Although the partially fixed atoms in the cylindrical shell could follow the vertical motion of the dynamic atoms in order to maintain the integrity of the crystal planes, there was also a possibility of sliding of the dynamic region relative to the shell. This “greasy” boundary condition was created in order to implement the experimental situation in which some of the grains could translate normal to the surface relative to the surrounding polycrystalline environment.

During the MD simulations, snapshots of the system were saved every 0.5 ns. They contained positions and velocities of all atoms, as well as the local mechanical stresses and energies. The stresses were computed using the standard virial expression and were later averaged over appropriate regions as discussed below. Several post-processing methods were applied to examine the evolution of grain shapes, GBs, atomic fluxes and stresses during the hillock growth. For a qualitative study of diffusion paths and grain translations, we employed a technique in which atomic groups were tracked by coloring. Atoms contained in a region of interest in a particular snapshot were identified, colored, and their new positions were examined in subsequent snapshots.

For a quantitative description of mass transport processes, integrated atomic fluxes were computed in the axial direction $z$ as well as in radial directions. The $z$-flux was computed by comparing atomic positions in two snapshots separated by a time interval $t$. To compute the integrated flux, an imaginary dividing plane parallel to the surface was placed at some position $z$ in the first snapshot, and atoms located on either side of the plane were identified. The new position of the dividing plane in the second snapshot was computed by including the Poisson effect. By
examining the new atomic positions of all atoms, the numbers of atoms that crossed the dividing plane by moving upwards and downwards were calculated. The difference \( \Delta N \) between these numbers, normalized by the total number of atoms \( N_{\text{tot}} \), was taken as the integrated net flux of atoms during the time interval \( t \) and was plotted as a function of \( z \). The goal of introducing the Poisson correction was to separate the rigid motion of the lattice sites due to the elastic deformation from the diffusive motion relative to the lattice. Since we are interested in the hillock growth relative to the surface, we take \( z = 0 \) at the current position of the surface. The surface position was identified with the average coordinate of the upper layer of the partially fixed atoms. This position changes with time according to the Poisson effect. The integrated \( z \)-flux is positive if more atoms diffuse up than down, and negative otherwise.

Similarly to the \( z \)-flux, we computed the radial flux. In this case, instead of dividing planes we used imaginary dividing cylindrical surfaces of a variable radius \( R \). The axis of the cylinders coincides with the axis of the simulation block. The radius \( R \) of the cylindrical surface for the second snapshot was scaled according to the current value of the biaxial compression. As above, the goal of this step was to separate the diffusion flux from lattice translations. The computed difference \( \Delta N \) between the numbers of atoms that crossed the walls of the cylinder from inside and outside, divided by \( N_{\text{tot}} \), is identified with the integrated radial flux. The latter is considered negative when more atoms diffuse towards the axis than away from it, and positive otherwise.

An initial attempt to simulate hillock growth was performed on a simulation block with the top of the fourth grain sliced off even with the upper surface of the tricrystal; in other words, with a tetrahedral shape seed grain flush with the surface. Such simulations did not lead to upward growth of the seed grain. Instead, the seed grain disappeared by the upward motion of GBs 1–4, 2–4 and 3–4. Clearly, in this case a reduction in the total GB area was the dominant driving force for the structure change. With this failure, we employed the full structure with the seed grain protruding above the tricrystal surface as shown in Fig. 3e. We will comment further on the seed grain in Section 4.

3. Results

We first describe the stress state of the simulation block produced by the radial compression, followed by analysis of the various diffusion fluxes encountered, and finally present images showing the movements of atoms that cause the hillock evolution.

3.1. Stress behavior

The bulk stress \( \sigma \) was computed by averaging over regions under the surface, i.e. excluding the protruding portion of grain 4. Only free atoms separated by at least 15 Å from the fixed, partially fixed and surface atoms were included in the calculation. The behavior of the axial (\( \sigma_{zz} \)) and lateral (\( \sigma_{xx} \) and \( \sigma_{yy} \)) components of the bulk stress as functions of time is illustrated in Fig. 5. (The lateral directions \( x \) and \( y \) are, respectively, parallel and perpendicular to the \( \Sigma5 \) GB plane.) Because the lateral strain rate is constant, the time axis in this plot is proportional to the total strain. After the biaxial compression is applied, the lateral stresses \( \sigma_{xx} \) and \( \sigma_{yy} \) remain similar and their magnitude increases with time. This increase continues during the first \(~10\) ns and then reaches a saturation. During this period of time, the deformation remains nearly elastic and the interatomic distances in the fixed and partially fixed regions constantly decrease. After \(~17\) ns of compression, significant plastic deformation begins, accomplished mostly by diffusive motion. At this point the lateral stress drops and the coherency between the dynamic atoms and the cylindrical shell (partially fixed atoms) breaks down. During the entire compression process, \( \sigma_{zz} \) remains small but contains important spatial gradients described below.

The presence of a small amount of plastic deformation was noticed at early stages of the compression process. For example, intrinsic stacking faults (SFs) appeared in grains 1, 2 and 3 during the first 5 ns of the simulations (Fig. 4). This is not surprising given that this interatomic potential predicts a relatively low SF energy, 44.4 mJ m\(^{-2}\), in good agreement with experiment (45 mJ m\(^{-2}\) [19]). No SFs were observed in the seed grain 4 due to the small level of stresses in this grain.

Fig. 6 shows the average lateral stress as a function of distance in the \( z \) direction. This stress was computed by averaging the \( \sigma_{xx} \) and \( \sigma_{yy} \) components over 15 Å thick layers normal to \( z \) that extended to the edges of the dynamic region (the fixed and partially fixed atoms were not included). The plot shows that the lateral stress is compressive (negative) in the lower part of the block, decreases in magnitude approximately linearly with \( z \) when approaching the surface, and
goes through zero near the surface. Note that the upper part of grain 4 is under some tension (positive stress) for reasons that are not apparent. The decreasing compressive stress as the seed grain is approached, combined with the different orientations of the GB planes, provides the gradients of the chemical potential that drive the GB diffusion processes described below.

We also computed the average lateral stress as a function of distance from the axis of the simulation block (Fig. 7). This stress was obtained by averaging over imaginary 15 Å thick cylindrical shells of different radii \( R \) and included only regions under the surface. This plot shows that the magnitude of lateral compression increases with distance from the axis of the simulation block. This stress gradient also contributes to the chemical potential gradients on GBs.

3.2. Atomic fluxes

Fig. 8 illustrates the integrated axial flux computed after 10, 20 and 30 ns of biaxial compression. The positive value of the flux reflects the predominance of the upward motion of atoms. Note that the flux remains positive even above the surface and becomes negative only in the upper part of the seed grain. The negative flux is caused by the surface diffusion from the top of the seed grain towards the surface of grains 1, 2 and 3. This diffusion flux tends to level the seed grain with the free surface and works against the growth of the grain upwards by stress-driven diffusion.

The integrated radial flux computed after 20 ns of biaxial compression is plotted as a function of \( R \) in Fig. 9a. The flux was computed separately for two regions: the lower part of the block below grain 4 and the upper part that includes grain 4. The plane separating the two regions is shown schematically in Fig. 9b. Note that the flux in the lower region is negative, meaning that more atoms diffuse towards the 1–2–3 TJ than away from it. By contrast, the flux computed for the upper region is positive (divergence away from the axis of the block) and has a greater magnitude than the flux in the lower region. The directions of the diffusion fluxes reconstructed from this plots are illustrated schematically in Fig. 9b.

3.3. Details of atomic movements

To reveal details of atomic movements during the evolution of our system, we colored and tracked atoms selected in various regions of the simulation block. The spreading and/or displacement of the colored atoms in the course of the simulations contained information about atomic fluxes and grain translations. The 3-D picture of the spreading and translation was often complex and required examination of multiple cross-sections of the simulation block. Fig. 10 shows several slices selected for presentation in this paper.

Fig. 11 demonstrates how atoms spread from a layer parallel to the surface, with the layer atom shown in blue. This layer was chosen in the lower portion of the block below the 1–2–3–4 junction point. Sections a and b reveal significant atomic diffusion towards the surface along the
1–2–3 TJ and the 1–2, 2–4 and 3–4 GBs. By contrast, sections c and d (which are perpendicular to each other and cross the 1–4 GB) show that diffusion along the 1–4 GB is negligible in comparison with other boundaries. The position of the 1–4 GB is marked in this figure by a dashed line and was identified by other visualization methods.

To reveal relative displacements of the grains, we selected colored regions in the shape of long parallelepipeds aligned either parallel or normal to the surface and crossing one or more GBs. The results for a parallelepiped parallel to the surface and running through grains 1, 2, 3 and 4 are displayed in Fig. 12a and b. The rigid upward displacement of the segment contained in grain 4 shows that this grain has translated relative to its polycrystalline environment and that this translation has a vertical component.

Fig. 12b confirms the extensive GB diffusion along the 2–4 GB and the lack of diffusion along the 1–4 GB (no smearing of colored atoms). The significant difference between the two GBs is further demonstrated by the vertical parallelepipeds displayed in Fig. 12c. The upper half of the right-hand-side parallelepiped shows a vertical displacement relative to the lower half, indicating that GB diffusion along the 2–4 boundary was accompanied by accretion of material to this boundary. This accretion produces the displacement of grain 4 which is evident from sections a and b.

Other sections (not shown here) reveal a similar accretion of material at the 3–4 GB. By contrast, the left-hand-side parallelepiped undergoes only a shear deformation of its shape without significant smearing. The shape deformation indicates a relative tangential translation of grains 1 and 4 accompanied by a displacement of the 1–4 GB without significant diffusion. Fig. 13 presents a more detailed view of this process, showing only the colored atoms and marking the initial and final GB positions. This process clearly exhibits all properties of the stress-driven GB motion coupled to shear deformation [20]. This observation further confirms the generality of the coupling effect [20] since this GB presents a mixed and asymmetric boundary that formed naturally as a result of structural evolution of the system. This boundary has a highly ordered (“coherent”) atomic structure with some of the crystal planes being continuous across the GB plane with a small angle of bending.

To compare the initial and final positions of grain 4, we superimpose thin sections of the first and last snapshots of the simulated system in Fig. 14. Both sections are 10 Å thick and go through the middle of grain 4. They are aligned so that the z-coordinates of the surfaces of the partially fixed regions in both snapshots coincide. This figure clearly demonstrates sidewise and upward growth of grain 4. This growth occurs by stress-driven diffusion and accretion of atoms to the 2–4 and 3–4 GBs, accommodated by coupled shear and displacement of the 1–4 GB. From the examination of various sections of the block, we find that the net displacement vector of grain 4 relative to the surface
is approximately \((-5\,\text{Å}, -5\,\text{Å}, 5\,\text{Å})\) during the 30 ns MD simulation. Note that by the end of the simulation, the sidewise growth of grain 4 resulted in its impingement on the boundary layer of partially fixed atoms. This prevented...
us from pursuing longer MD simulations using this simulation block.

4. Discussion and conclusions

The MD simulations reported in this paper reveal a number of processes that can occur in a polycrystalline film at elevated temperatures under an applied in-plane stress. We were particularly interested in initial stages of the growth of hillocks and whiskers, a process in which a protrusion grows by addition of material to its root. We emphasize that this process is different from other growth phenomena that have recently been simulated by MD, such as the nanowire growth by the vapor–liquid–solid mechanism in which the nanowire grows by accretion of material on its top [21].

The particular four-grain configuration created for this study mimics the experimental structures which are believed to be responsible for the nucleation and growth of hillocks and whiskers in deposited layers (see e.g. Fig. 1). This structure contains a seed grain exposed to the free surface and in contact with other grains and TJs underneath the surface. Although the simulations were performed on a specific material (Cu) at a relatively high temperature suitable for MD simulations, our findings are believed to be rather generic and can be relevant to hillock/whisker growth in Sn electrodeposits and other systems. Some of the processes observed in this study promote the growth of the seed grain into a hillock or a whisker, others stifle the growth. The growth requires a proper balance between at least four processes: (1) surface diffusion, (2) internal GB motion, (3) diffusion and accretion of material on GBs, and (4) GB sliding/shear. We will discuss these processes in turn.

In general, surface diffusion opposes the formation of hillocks. If surface diffusion is too fast, the GB flux from the interior towards the free surface in response to gradients of normal stresses on GBs will be spread too widely across the free surface and no localized accumulation of material will occur. This trend was certainly observed in our simulations. For example, Figs. 8 and 9 show that the mass fluxes at the surface and near the top of the seed grain are dominated by lateral and downward components which tend to reduce or even suppress the material buildup at the surface. Fig. 14 also clearly reveals the shape change due to the lateral spreading of the material. In fact, we were forced to halt the simulations when the lateral spreading of the hillock reached the partially fixed atoms at the edges of the simulation block. One possibility suggested in the literature that might reduce the surface diffusion and thus promote hillock growth is the presence of a thin oxide film. Future MD simulations may examine how a surface diffusion inhibitor can assist the development of a hillock.

No hillock growth was observed in the simulations without a protruding seed grain, i.e. when grain 4 was cut off even with the surface. During the MD simulations with and without applied stresses, the remaining part of the seed grain quickly shrank and disappeared by capillary-driven GB motion. Specifically, the three internal GBs (1–4, 2–4 and 3–4) bounding the tetrahedral grain 4 were found to rapidly migrate towards the grain center, consuming the grain until it disappeared. This produced a tricrystalline structure with the 1–2–3 TJ terminating at the surface. Subsequent MD simulations under stress did not detect any local accumulation of material in the TJ/surface region that would result in the formation of a hillock. Thus, a seed grain protruding above the surface was necessary for obtaining a hillock growth in our simulations. This protrusion effectively pinned the 1–4, 2–4 and 3–4 GBs at the free surface. If simulations had been performed with a seed grain bounded by more than six faces, it is possible that the grain might have survived without requiring an initial protrusion to pin the GBs. This would be similar to the situation in exaggerated grain growth. Such a simulation was beyond the scope of the present paper and would present a challenge to the MD methodology. It is to be noted that in experiment, many hillock grains of Sn appear to have more than six sides exposed to the substrate as shown in the top view in Fig. 1. Furthermore, the faces of the large hillock grain as seen in the cross-section clearly eat into the finer-grained columnar structure of the deposit. The relationship between the GB migration and the upheaval of the hillock grain requires further investigation.

Another possibility for the survival of a non-protruding seed grain might be to create a sufficiently high accretion rate on internal GBs to overwhelm the GB curvature effect. Indeed, a preferential accumulation of material (or condensation of vacancies) on one side of a GB can drive its motion against curvature and create stresses pushing the adjacent grains apart in the normal direction. This mechanism is responsible for the upward and sidewise movements of grain 4 observed in our simulations. If grain movements are constrained, local back-stresses can arise that can decrease the chemical potential gradients and eventually shut down the driving force for the GB diffusion fluxes towards the growing hillock. Only further analysis, modeling and experimentation can substantiate this speculation.

During the creation of the initial equilibrium four-grain structure, the seed grain rotated to form at least one “special” GB (1–4). This boundary has a “coherent” structure with continuous and slightly bent crystal planes. It is likely to have a relatively low energy and is characterized by a much slower diffusivity than other boundaries present in the system. While diffusion fluxes were clearly observed in the other 5 GBs, no diffusion and consequently no accretion was possible on this “special” boundary. First, the absence of accretion may have contributed to the failure to stabilize a non-protruding grain as described above. More importantly, the absence of diffusion on the “special” GB and the presence of accretion on two other GBs (2–4 and 3–4) bounding the seed grain created a shear stress on the 1–4 GB. As a result, upward motion of grain 4 was only possible if sideways motion occurred on the 1–4 GB. In response to this shear stress, this boundary was observed to move by...
the coupling mechanism [20] producing a shear deformation and thus the needed tangential displacement of the grains. In the present simulation geometry, the pinning of the 1–4 GB by the external surface groove has limited the amount of coupled motion and eventually led to a stalling of the hillock growth.

From these simulations, we can conclude that (1) the relatively easy rotation of a seed grain in contact with the free surface may increase the variability of GBs and create “special” boundaries with low diffusivity; (2) this variability can further lead to unequal accretion of material at different GBs and thus produce internal stresses; and (3) these stresses can be (at least partially) accommodated by stress-induced coupled motion of GBs leading to grain translations and possibly additional rotation. The relative importance of these factors can be material-dependent. In the case of Sn hillock growth, it is not immediately clear whether Sn with its non-cubic structure would be less likely to form low-energy grain boundaries with poor diffusivity. Whether Sn with its non-cubic structure would be less likely to form low-energy grain boundaries with poor diffusivity.

But for a time of 1 s, the same calculation gives the diffusion path of 2 μm. In room-temperature experiments, Sn whiskers as long as a few micrometers can indeed grow in minutes. These estimates show that the seemingly small growth amounts observed on the time scale of MD simulations can translate to very significant growth amounts under experimental conditions.

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