Planarization in Electrochemically Fabricated Nanodimensional Films

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Recent demonstrations of electrochemical fabrication of nanodimensional, alternating metal and metal oxide films open a pathway to nanoscale templating with high-quality interfaces and high uniformity over macroscopic surface areas. Planarization during electrochemical oxidation is the critical enabling feature of this growth process. Here we present a theory and simulation of this planarization phenomenon applicable to a wide range of initial surface profiles and material systems. We describe the impact of different system parameters on the rate of planarization for both the exposed oxide surface and the internal metal oxide interface. Finally, we show that our simulations are consistent with experimental measurements of Ta2O5 electrochemically grown on Ta thin films.

Introduction and Background

The recent demonstration by Mardilovich and Kornilovitch of the atomic-scale, large-area planarization process in the electrochemical growth of multilayer, nanodimensional alternating metal and metal oxide thin films indicates potential use of these structures as nanoscale templates similar to the GaAs/AlGaAs multilayer stacks employed by Natelson et al.,2,3 Melosh et al.,4 and Austin et al.5 To be suitable for such applications, the multilayer films must have the following properties: (1) the layer thickness must be reproducible and controllable with nanometer precision; (2) sub-nanometer root-mean-square roughness at the interface. Third, the constituent layers should have distinctly different etch rates so that following growth of the multilayer stack, a sharp pattern can be etched into the edge of the stack to form a desired template. In ref 1 was shown that multilayer stacks of alternating Ta and electrochemically grown Ta2O5 have all of these properties and stacks of up to 10 layers, with pitches ranging from 200 nm down to 12 nm and a minimum layer thickness of 2.8 nm, were demonstrated. Ta/Ta2O5 stacks of up to 24 layers were later fabricated on 6-in. wafers, demonstrating large-area reproducibility of the process.6 The critical mechanism enabling these results was found to be the concurrent planarization of the metal and oxide films during electrochemical oxidation.

In this paper we quantitatively investigate the planarization process. We report additional experimental analysis of the electrochemically grown Ta2O5 thin films to compare it to our theoretical model and associated numerical simulation of oxide growth. We show that our numerical analysis closely reproduces the experimentally observed planarization phenomenon. We also describe the impact on planarization of the initial roughness of the metal surface and the expansion coefficient of the oxide (relative to the metal), allowing these results to be extended to other metal oxide systems (e.g., Al–Al2O3, W–WO3, Nb–Nb2O5).

Theory and Model

The theory of electrochemical oxidation is well-known and provides the basis for our analysis of the planarization process. In this work, as in ref 1, thin Ta metal films are deposited by direct current (DC) sputtering onto a flat substrate (Si wafers or coupons with a layer of 1.7 μm thermally grown SiO2 or silicon nitride grown by low-pressure chemical vapor deposition with thicknesses from 0.12 to 0.3 μm), and the samples are then placed in a 0.01% solution of citric acid (C6H8O7). The Ta film functions as an anode and a platinum counter electrode as a cathode (reference electrode was not used). A computer-controlled Keithley 2400 DC power supply was used to apply the required constant current density or constant voltage. In general, when DC is applied, anodic oxide builds by diffusion of metal cations (Ta5+, Al3+, W6+, etc.) and O2– anions in opposite directions. The rate of oxide layer growth is proportional to the current density and is steady in the galvanostatic regime. There is a linear correlation between the thickness of the oxide layer and the final applied voltage. For details, see ref 1. The potential drops principally across the growing oxide film, and as a result, one observes stronger electric fields in the thinner regions. Since the flow of the charged oxide reactants (i.e., O2– and Ta5+) through the oxide layer is driven by this field, the oxide grows more rapidly in the thinner regions. As
a result, the oxide layer grows conformally, i.e., maintaining the same thickness everywhere. The conformal nature of the growth is illustrated in Figure 1. Such conformal growth is known to "self-heal" variations in film thickness, leading to planarization for oxide thicknesses exceeding the peak-to-valley magnitude of the initial film roughness. This is indicated in Figure 2 (reproduced from ref 1), which shows typical AFM data for the electrochemically grown Ta$_2$O$_5$ surface as a function of oxide thickness. It should be noted that the anodization process is fundamentally different from thermal oxidation (which can occur with, for example, tantalum and tungsten) and corrosion. With thermal oxidation and corrosion the oxide growth is not conformal and planarization would not take place.

The planarization of a rough metal surface by a conformal growth process is explained qualitatively by considering two cases: anodization of a metal hill and a metal depression. To form a layer of oxide on a metal hill having a constant perpendicular oxide thickness, the relatively sharp point of the hill must become concentric circular sections in the oxide and underlying metal surfaces and similarly for the metal depression. A schematic illustration of both cases is shown in Figure 3 for the typical case that the expansion coefficient, $k_{ex}$, is greater than 1 (specifically, $k_{ex} = 2.3$ for conversion of Ta into Ta$_2$O$_5$.) The quantity $k_{ex}$ is defined as the ratio of the volume of oxide grown to the volume of metal consumed and is sometimes called the Pilling—Bedworth ratio.

This essentially geometric argument can be alternatively explained in terms of physical principles. Around a metal peak, there is a larger area of oxidizable surface relative to the volume of underlying metal. As a result relatively more metal will be consumed at the peak than on the sides of the hill to form the needed thickness of oxide, which will cause the hill to flatten. The inverse process operates around a metal depression, where there is a smaller area of oxidizable surface relative to the volume of underlying metal. As a result, relatively less metal will be consumed at the base than on the sides of the depression to form the needed thickness of oxide, which will cause the depression to flatten.

Further insight can be obtained by treating the idealized situations shown in Figure 3 quantitatively. The original metal hill is symmetric and terminates with a rounded apex of radius $R_0$. As anodization proceeds, the top and bottom interfaces grow away from each other while remaining a distance $d$ apart at any surface point. On the flat regions, the conservation of metal volume yields

$$d_1 = \frac{(k_{ex} - 1)}{k_{ex}} d \quad d_2 = \frac{1}{k_{ex}} d$$

(1)

where $d$ is the total oxide thickness. In the apex area, the two interfaces have constant curvature with radii $r$ and $R$ for the bottom and top surfaces, respectively. The radii always satisfy $R = r + d$. Another relation is given by conservation of volume

$$k_{ex} V_{\text{consumed metal}} = V_{\text{oxide}}$$

(2)

Explicit expressions depend on whether the hill is ridgelike or conelike, i.e., the geometry is uniform in the direction perpen-
characteristics can easily be found. For example, the rising

\[ \Delta z_{\text{top}} = \frac{(r + d_2 - R_0)}{\cos \theta} - r + R_0 \]  

Similarly, the lowering of the top point of the internal interface is

\[ \Delta z_{\text{bottom}} = \frac{(r + d_2 - R_0)}{\cos \theta} - r + R_0 \]  

Figure 4a shows the two radii and the two \( \Delta z \) values for \( \theta = 40^\circ = 40\pi/180 = 0.698 \text{ rad} \), \( k_{\text{ex}} = 2.3 \), and \( R_0 = 2.0 \text{ nm} \) for the ridge geometry. Once \( d > R_0 \), the radii grow proportionally to the oxide thickness. \( \Delta z_{\text{top}} \) and \( \Delta z_{\text{bottom}} \) are also roughly proportional to \( d \), however, \( \Delta z_{\text{top}} \) is much smaller than \( \Delta z_{\text{bottom}} \), which indicates that surface roughness decreases with \( d \).

Analysis of the function \( r(d) \) reveals that at large enough angles the inner radius actually decreases with the oxide thickness and at some point reaches zero. Setting \( r = 0 \), the critical thickness is obtained as follows

\[ d_c(r = 0) = k_{\text{ex}}R_0\sqrt{\tan \theta - \frac{\tan \theta - \tan k_{\text{ex}}\theta}{\tan \theta - k_{\text{ex}}\theta}} \]  

This quantity becomes imaginary at an angle defined by the condition

\[ \frac{\tan \theta}{\theta} = k_{\text{ex}} \]  

For Ta \( (k_{\text{ex}} = 2.3) \), \( \theta_c = 70^\circ \). Thus for \( \theta < \theta_c \), the regime \( r = 0 \) is never reached, and \( r(d) \) grows indefinitely. For \( \theta > \theta_c \), the regime \( r = 0 \) is reached at \( d = d_c \). After that, the inner radius remains zero and the volume conservation condition should be reformulated in terms of the outer radius \( R \) alone.

Planarization of a metal depression can be analyzed in a similar fashion, see Figure 3. In the ridge geometry, the oxide and metal volumes are given by

\[ A'B'C'D' = \theta(R^2 - r^2) = \theta(2r'd + d^3) \]  

(oxide, ridge depression geometry) (10)

\[ E'B'C'F' = \theta[(r' + d)^2 - R_0^2] - \tan \theta[(r' + d)^2 - R_0^2] \]  

(metal, ridge depression geometry) (11)

Substitution in the volume conservation relation again leads to a quadratic equation for \( r \), with a solution

\[ r' = -d\left(\frac{k_{\text{ex}} - 1}{k_{\text{ex}}} + \sqrt{\frac{d^2}{k_{\text{ex}}^2} - \frac{\theta}{\tan \theta - \theta + R_0^2}} \right) \]  

If \( \theta > \theta_c \), where \( \theta_c \) is determined from the equation

\[ \frac{\tan \theta_c}{\theta_c} = \frac{k_{\text{ex}}}{k_{\text{ex}} - 1} \]  

(\( \theta_c = 63^\circ \) for \( k_{\text{ex}} = 2.3) \), then the inner radius reaches zero at a critical oxide thickness

\[ d'(r' = 0) = R_0\sqrt{\frac{\tan \theta - \frac{\tan \theta - \tan k_{\text{ex}}\theta}{\tan \theta - k_{\text{ex}}\theta}}}{\tan \theta - \left(\frac{k_{\text{ex}} - 1}{k_{\text{ex}}}\right)^2 - \theta\left(\frac{k_{\text{ex}} - 1}{k_{\text{ex}}}\right)} \]  

The formulas for the depression geometry can be obtained from the corresponding formulas of the hill geometry by a substitution \( k_{\text{ex}} \rightarrow k_{\text{ex}}/(k_{\text{ex}} - 1) \). Typical behavior of the system’s parameters is shown in Figure 4b. In contrast with the ridge hill geometry,
\( \Delta z_{\text{top}} \) now grows much faster than \( \Delta z_{\text{bottom}} \), thus indicating planarization of the depression.

In the conelike case, the metal and oxide volumes are those of spherical segments defined by a polar angle \( \theta \). The algebra is more cumbersome in this case, and analytic expressions for the system parameters cannot be obtained in a closed form. However, numerical analysis reveals the same qualitative smoothing behavior with oxide growth.

The discussion so far has been concerned with just one nonflat region, either peak or depression. In a real situation those two types coexist together, as illustrated in Figure 3. For small oxide thicknesses, the developments of the two areas proceed independently, in accordance with the formulas derived above. However, at a certain thickness the two points B and A’ will collide, and the roughness decrease will start following a more complex law. This “confluence” thickness can be determined from the following condition

\[
(r' + d_1)\tan(\theta/2) + (r + d_2)\tan \theta = \frac{Z_0 + (R_0 + R'_0) \left( \frac{1}{\cos \theta} - 1 \right)}{\sin \theta} \tag{15}
\]

where \( Z_0 \) is the original Z range of the surface. The quantities \( r, r', d_1, \) and \( d_2 \) should be understood as functions of the total oxide thickness \( d \). For example, for \( \theta = 40^\circ \), \( k_{\text{ex}} = 2.3 \), \( R_0 = R'_0 = 2.0 \text{ nm} \), and \( Z_0 = 100 \text{ nm} \), the above equation yields \( d_{\text{confluence}} = 82 \text{ nm} \). Note that we use the total \( Z \) range of the surface, i.e., the ridge-to-depression height, as a measure of surface roughness. In Figure 4c, we show the surface roughness calculated for the above set of parameters. The solid line indicates a direct calculation up to the confluence thickness; the dashed line shown for larger oxide thicknesses is a cartoon approximation of the subsequent behavior.

To move beyond this simple analytic treatment we perform finite element numerical simulations of the oxide growth process for arbitrary initial surfaces. First we create a grid of equally spaced points in the \( xy \) plane having arbitrary \( z \) values, representing the initial metal surface. A virtual point is defined in the center of square defined by the \( xy \) grid, and the height of this virtual point is obtained by averaging the \( z \) value at the four corners. The union of this point and the two points on each side of the square define four triangular facets that formally comprise the discretized model surface. This construction is illustrated in Figure 5.

Second, we define an oxide surface on the \( xy \) grid, such that the space between the oxide surface and the metal surface defines the oxide film. Initially, this oxide surface is identical to the metal surface. The simulation proceeds by selecting the point in the system where the oxide film is thinnest and oxidizing a small amount of metal at that point. When many points in the system correspond to the minimum oxide thickness (as is initially the case), the point is randomly chosen from among these minimum thickness points. The simulation then continues until a target maximum oxide thickness is obtained by at least one point in the system. The critical simulation tasks are: (1) the maintenance of material conservation given a particular oxide expansion coefficient, \( k_{\text{ex}} \); and (2) the calculation of the oxide thickness at each point. The former is evaluated using the result (obtained from geometric arguments) that the volume contained under the metal surface for a given \( xy \) grid square is given by

\[
V_p = \frac{1}{4} c^2(z_1 + z_2 + z_3 + z_4) \tag{16}
\]

where \( c \) is the \( xy \) grid spacing and \( z_0 \) represent the four \( z \) values at the corners of the grid square. As a result, the change in volume of the metal and oxide films is proportional to the change in the individual point, regardless of the values of the surrounding points. Therefore, to maintain volume conservation during oxide growth, when one lowers a metal point by an amount \( \Delta z \), one increases the corresponding oxide points by a total amount \( (k_{\text{ex}} - 1)\Delta z \). To calculate the oxide growth, the distance between the metal point and each surrounding oxide point and the lines connecting those oxide points are considered. (For computational efficiency we neglect the second order corrections obtained by including metal point to oxide plane distances.)

In carrying out actual simulations, a sufficiently small oxide step size is employed such that further reductions in this step size do not change the observed results. Also, we find that it is necessary to oversample the initial surface grid by a factor of 4 in the \( x \) and \( y \) directions (yielding 16 times the original number of grid points) to obtain accurate results. The simulation is implemented using the current version of MATLAB, running on a 3.2-GHz Pentium 4 under Windows XP.

**Experimental Input to the Surface Roughness Model**

We report new experimental data on Ta/Ta\(_2\)O\(_5\) thin film electrochemical oxidation utilizing transmission electron microscopy (TEM), atomic force microscopy (AFM), and scanning electron microscopy (SEM) to analyze Ta metal films and Ta/Ta\(_2\)O\(_5\) film pairs at different stages of oxidation. TEM measurements were performed on four samples: (1) 1-\(\mu\)m Ta; (2) 1-\(\mu\)m Ta with 37 \(\mu\)m of anodized oxide; (3) 0.2-\(\mu\)m Ta; (4) 0.2-\(\mu\)m Ta with 16 \(\mu\)m of anodized oxide. The Ta metal films were grown as previously described in ref 1. For TEM the samples were coated with carbon, chrome, and platinum before preparing FIB cross sections. The images were obtained in the Scanning TEM (STEM) mode, using a JEM 2500 TEM with 200 kV accelerating voltage. STEM mode was chosen to amplify the diffraction contrast from grains and defects relative to the normal TEM imaging mode. Results for the 1-\(\mu\)m Ta sample are shown in Figure 6, clearly showing the presence of deep cracks in sputtered Ta films. These cracks have a depth of 50–100 nm and a width of 3–10 nm. Because of their nanoscale widths, we have termed them “nanocracks” or “spikes”. We have also found that in the anodized samples the spikes are entirely absent on the top oxide surface but still observable in the underlying...
metal layer. We conclude that the spikes are rapidly filled during oxidation such that the oxide surface is spike-free for even very small oxide thicknesses. At the same time, the spikes in the underlying metal persist until the depth of metal consumed during oxidation is equal to the spike depth.

Tapping-mode AFMs measurements were also performed on as-deposited Ta metal films, using Digital Instruments D3100 AFM in the open loop mode and scan sizes of $(200 \times 200)$ nm² and $(2 \times 2)$ μm². The AFM data does not indicate the presence of spikes, reflecting the inability of the AFM tip to resolve such deep, narrow surface features. In addition, the data does reveal three additional distinct roughness scales on the Ta surface. Thus our surface roughness model comprises the following features, illustrated in Figure 7: (1) “spikes” of $3-10$ nm in width and $50-100$ nm in depth; (2) random roughness with a peak-to-valley amplitude of $3-10$ nm and a period of $10-20$ nm (“random”); (3) small curved grains between spikes (“grain”) of height $8-20$ nm and width $40-100$ nm; and (4) large curved grains of height $20-50$ nm and width $200-500$ nm (“large grain”).

As mentioned in the previous section, we also performed SEM (SEM-FIB, FEI/Philips XL 30-S SEM) measurements on oxidized Ta films. These measurements clearly revealed the conformal nature of the Ta₂O₅ electrochemical growth process (see Figure 1).

Results and Discussion

We performed a series of simulations of conformal surface oxidation to investigate the critical parameters governing the planarization process. Figure 8 illustrates the overall character of the simulated smoothing process by depicting the profile of a surface with initial “random” roughness (a) and of the surface after growth of 10 (b), 20 (c), and 30 (d) nm of oxide. In these calculations we have used $k_{ex} = 2.3$, which corresponds to electrochemically grown Ta₂O₅. The “random” initial roughness is obtained by assigning random offsets to the initial metal thickness (here 200 nm) uniformly over the interval of $-1.5$ to $1.5$ nm to each grid point with a grid point spacing of 4 nm. In this example, a total sample area of 36 nm by 36 nm is simulated.

The smoothing of the oxide surface can be evaluated more quantitatively by plotting the root-mean-squared (rms) roughness of the surface as a function of oxide thickness, as shown in Figure 9a for each of the initial roughness elements present in the roughness model described in the previous section. For the “random,” “spike,” and “grain” elements, a 4 nm spaced grid covering an area of 36 nm by 36 nm is simulated. The “random” system is constructed as described in the previous paragraph (i.e., each point given a random offset over the interval of $-1.5$ to $1.5$ nm). The “spike” element consists of a 50 nm negative offset to the central grid point of the system. The “grain” element consists of an offset given by

$$-8 \cos \left[ \frac{x^2 + y^2}{2 \times 18 \sqrt{2}} \right]$$

relative to the initial metal surface, where the origin is taken as the center of the grid. For the “large grain” element, a 28 nm spaced grid covering an area of 280 by 280 nm is simulated, with the initial surface given by

$$-25 \cos \left[ \frac{x^2 + y^2}{2 \times 140 \sqrt{2}} \right]$$

relative to the initial metal surface, where the origin is again taken as the center of the grid. The roughness of the internal metal surface as a function of oxide thickness for each of these systems is also obtained from the simulation, as shown in Figure 9b. For the exposed oxide surface, we find that, for all of the features in our model, it is the lateral dimension of the feature that dominates how rapidly the surface planarizes, i.e., in general, a feature having a lateral dimension of X will require oxide growth of roughly X to planarize. For the internal metal surface, the same behavior is observed for the “random,” “grain,” and “large grain” features; the “spike” feature, however, requires more than 100 nm of oxide thickness before it is planarized and illustrates an important exception to this simple rule: for features that have a larger vertical than lateral feature size, the vertical dimension can become of the dominant factor in the planarization rate. Specifically, to planarize a deep, narrow depression (of which the “spike” is one example), one requires an oxide thickness which is roughly the feature depth multiplied by $k_{ex}$, because the feature persists until sufficient metal is consumed to absorb the depression. Though we have not investigated the symmetric case of a tall, narrow hill, similar logic suggests that the oxide surface will not entirely planarize until a thickness of oxide at least equal to the initial feature height multiplied by $k_{ex} / (k_{ex} - 1)$, is grown.

These simulations are computationally intensive, requiring multiple days to complete and having run times that scale as the number of grid points. As a result, it was not possible to directly simulate both the relatively small scale “random,” and “spike” and “grain” features along with the relatively large scale “large grain” feature. We therefore investigated how well a simple sum-of-squares approximation of the roughness values
obtained for individual model elements reproduces the behavior of a directly simulated combination of the same model features. The results of this calculation are shown in Figure 10, which shows simulation results for the exposed oxide surface for the individual “random,” “spike,” and “grain” features, along with the directly simulated combination of these three features (i.e., “random + grain + spike”) and a sum-of-squares approximation obtained by taking the square root of the sum of squares of each of the individual model components. We find that the sum-of-squares approximation slightly overestimates the total roughness but otherwise well reproduces the result of the directly simulated system. Thus we conclude that to obtain, for instance, the rate of planarization for the “large grain + grain + random” system, we can apply a sum-of-squares approximation to the individual “large grain” and “grain + random” simulations, which are individually computationally feasible, whereas the combined system is not. It is worth noting that the rationale for

Figure 8. Simulated planarization of oxide surface for an initial metal film with “random” roughness (see Figure 8), following electrochemical oxidation ($k_{ex} = 2.3$). (a) Initial metal surface; (b) 10 nm oxide; (c) 20 nm oxide; (d) 30 nm oxide. (Note that color scheme is rescaled to the minimum and maximum height in each plot.)

Figure 9. Simulated rates of planarization by electrochemical oxidation, in terms of rms roughness and Z range (i.e., the difference between the minimum and maximum surface points), for the exposed oxide (a, c) and internal metal (b, d) surfaces. Four different initial metal film features (as defined in Figure 7) are modeled, and $k_{ex}$ is set to 2.3. Note the marked difference in the planarization of the “spike” for the oxide and metal surfaces and the substantially larger impact the “spike” feature has on the Z range as compared to the rms roughness.

Figure 10. Planarization by electrochemical oxidation ($k_{ex} = 2.3$) of initial metal surfaces having different initial roughness model components as a function of oxide growth. Note the comparison between a sum of squares approximation of the random + grain + spike system (obtained by taking the square root of the sum of the squares of the individual random, grain and spike simulation data) and a direct simulation of this system.
the sum–of–squares approximation comes from the observation that independent random variations in surface roughness contribute to the overall rms roughness through a sum–of–squares dependence. Thus the success of this approximation is an indication that the individual roughness elements contribute to the total roughness approximately independently. Our results also indicate that the total roughness of a sample is dominated by whichever model feature has the greatest roughness at a given oxide thickness, so that in our model, the vast majority of the planarization process is due to the “large grain” feature, with the other features only slightly impacting the planarization occurring at the very beginning of the growth process.

While we have focused on \( k_{\text{ex}} = 2.3 \) because of our interest in the Ta\(_2\)O\(_5\) system, we have also performed simulations of the planarization process for \( k_{\text{ex}} \) equal to 1.3 and 3.3 as well, which approximately correspond to expansion coefficients for Al–Al\(_2\)O\(_3\) and W–WO\(_3\) systems. Such a significant difference in \( k_{\text{ex}} \) between Al\(_2\)O\(_3\), Ta\(_2\)O\(_5\), and WO\(_3\) stems from the different densities of corresponding oxides and metals. As an example, the densities of W and WO\(_3\) are 19.25 and 7.2 g/cm\(^2\), respectively, and the volume of one mole of WO\(_3\) is 32.2 cm\(^3\), which consumes 9.55 cm\(^3\) of W upon oxidation. The ratio of two volumes is 3.37. In real systems the values may differ slightly from these handbook numbers. Furthermore, \( k_{\text{ex}} \) calculated from densities can be used in analysis of planarization only if the oxide is not dissolved in electrolyte during anodization. To prevent such dissolution, we have used only those electrolytes in which the anodic oxides are chemically stable. These results, with the illustrative “grain” and “spike” systems shown in Figure 11, indicate that the expansion coefficient has only a weak impact on the rate of planarization of the exposed oxide surface. Stated differently, we conclude that it is the conformal nature of the oxide growth, and not the expansion of the oxide relative to the metal, that leads to planarization. However, it is worth noting that the planarization of the internal metal surface for the “spike” system has a strong dependence on \( k_{\text{ex}} \), because, as noted above, the rate (in terms of oxide thickness) at which this feature is consumed is inversely proportional to \( k_{\text{ex}} \). As a result, for larger and larger \( k_{\text{ex}} \), less and less metal is consumed to grow the same amount of oxide, and thus the more oxide one must grow to planarize the feature.

As above, we argue that this is a general characteristic of deep, narrow surface depressions.

Finally, we compare our simulation results to the experimental rms roughness data obtained from electrochemically grown Ta\(_2\)O\(_5\) films, as shown in Figure 2. Because of the computational difficulty of the planarization simulations, it is not practical to perform a simulation employing the entire raw AFM data as the initial surface profile because the number of data points is too large. We instead employ our model features, in conjunction, where necessary, with sum–of–squares approximations. These results are shown in Figure 12, in which we plot the simulation results for the “grain + random + spike,” “grain + random,” and “large grain” systems, along with sum–of–squares approximations of the “large grain” feature with the two other combined systems. As expected, the “large grain” behavior dominates, and on its own already provides an excellent fit to the experimental data; inclusion of the “grain + random” system in the first approximate sum (“without spike”) improves the fit at small oxide thickness even further. Because the experimental AFM data does not probe the nanocrack (aka “spike”) features, their influence on the roughness is not taken into account in the experimental numbers. However, we include for illustrative purposes the simulated behavior of the rms roughness in the presence of these nanocracks through the inclusion of the “grain + random + spike” system in the second approximate sum (“with spike”); the result is a small by noticeable increase in the roughness at small oxide thicknesses.

**Summary**

We have presented a theory of surface planarization in the course of electrochemical oxidation (anodization). For the simplest geometries of symmetric ridge and depression, analytical expressions have been developed based on the relation between the volumes of consumed metal and formed oxide and on the condition of constant oxide thickness. Analysis has shown a sharp decrease of the key roughness parameter, the peak–valley height difference, as a function of oxide thickness. We have also developed a numerical simulation algorithm to analyze arbitrary initial surfaces with variable feature sizes. The
algorithm provides roughness of both the top and bottom interfaces and allows studying the impact of feature geometry and expansion coefficient on the rate of planarization. The simulation results have been found to be consistent with experimental data for the planarization of the exposed oxide surface. The simulation has also proven useful in providing insight into processes that are otherwise difficult to access experimentally, including the impact of nanocracks on planarization and the rate of planarization of the internal metal surface. Finally, the techniques developed here provide a straightforward and powerful way to predict the roughness of both the top and bottom surfaces, using as input only easily accessible properties of a given metal-oxide system, i.e., the initial surface morphology and the oxide expansion coefficient.

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