Thermal stability of Cu nanowires on a sapphire substrate
Hongwei Li, Jeffrey M. Biser, Jason T. Perkins, Sreya Dutta, Richard P. Vinci, and Helen M. Chan

Citation: Journal of Applied Physics 103, 024315 (2008); doi: 10.1063/1.2837053
View online: http://dx.doi.org/10.1063/1.2837053
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/103/2?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Investigation of the thermal stability of Cu nanowires using atomistic simulations
J. Appl. Phys. 115, 213518 (2014); 10.1063/1.4876743

Thermal stability of Ti, Pt, and Ru interfacial layers between seedless copper and a tantalum diffusion barrier

Cu film thermal stability on plasma cleaned polycrystalline Ru
J. Vac. Sci. Technol. B 30, 052203 (2012); 10.1116/1.4742906

Self-organized Cu nanowires on glass and Si substrates from sputter etching Cu/substrate interfaces
J. Vac. Sci. Technol. B 24, 592 (2006); 10.1116/1.2172249

Thermal stability of Ti-catalyzed Si nanowires
Appl. Phys. Lett. 82, 263 (2003); 10.1063/1.1534616
Thermal stability of Cu nanowires on a sapphire substrate

Hongwei Li, a) Jeffrey M. Biser, Jason T. Perkins, Sreya Dutta, Richard P. Vinci, and Helen M. Chan

Center for Advanced Materials and Nanotechnology (CAMN), Department of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, USA

(Received 20 September 2007; accepted 21 November 2007; published online 31 January 2008)

Cu nanowires with widths ranging from 110 to 300 nm were fabricated on a c-plane sapphire substrate using E-beam lithography and lift-off processes. Thermal annealing of these polycrystalline metal nanowires at 700 °C in an inert (nitrogen) atmosphere showed that for lines of width 160 nm or less, there was complete breakdown into widely spaced, individual beads in a short time (1 h). It was shown that the morphological changes were driven by reduction in the surface energy, with surface diffusion as the predominant transport mechanism. The spacing between the beads was approximately 1.8 times greater than the values predicted by Rayleigh instability theory for a free standing rod with equivalent radius. Based on thermodynamic and kinetic considerations, discrepancies between the experimental observations and the predictions of Rayleigh instability theory were attributed to the stabilization effect of the substrate. © 2008 American Institute of Physics. [DOI: 10.1063/1.2837053]

I. INTRODUCTION

Nanowires are of technological interest due to their potential applications as interconnects as well as essential components in nanoelectronics or nanoelectromechanical systems (NEMS).1 The shrinkage of feature sizes down to the nanometer scale increases their susceptibility to morphological change, even at relatively low temperatures. At elevated temperature, shape changes in nanowires can be severe and occur rapidly.2 This is a critical issue for the long term reliability of nanoelectronic devices. It is expected that in addition to temperature, factors such as substrate and nanowire composition, the microstructure, cross-sectional geometry, and dimensions of the nanowires will all play roles in determining the degree to which morphological change happens. Therefore, it is important to determine which characteristics are the most critical so that the extent of undesirable morphological changes can be limited or avoided altogether.

Morphological instability of metal films and freestanding wires is a well-known phenomenon. For example, dewetting of blanket Cu thin films on dielectric substrates such as SiO2 has been reported, leading to balling up of the metal into discrete droplets.4-6 The thermodynamics and kinetics of this type of film agglomeration have been reviewed by Srolovitz and Goldiner.1 As described by these researchers, a series of agglomeration processes occurs, driven by a reduction of the surface and interface energy. First of all, there is the formation of small grooves, then these grooves deepen via various transport processes until they reach the substrate. Subsequent formation of holes separates the films into discrete parts, and the retraction and coarsening of these separated sections form individual droplets. Key characteristics that control the rate and nature of film breakdown include the interfacial energy between the film and substrate, and the film grain structure.

In a similar fashion, surface energy-driven breakdown of free standing wires has been analyzed by Nichols and Mullins, who applied Rayleigh instability concepts, originally developed to study the beading phenomena of liquid jets,7 to predict the shape changes of cylindrical solid rods.9 Their model assumed orientation-independent surface and bulk properties. Under these conditions, it was shown that any perturbation of the surface with a wavelength larger than the circumference of the rod could lead to breakdown given sufficient time. Here, the key parameter was simply surface curvature, which is directly related to wire geometry and size. The relevance of this model across a wide range of length scales was recently demonstrated by Toimil Molares et al.,2 who annealed free standing Cu nanowires placed on silicon substrates and showed that the beading phenomenon conformed closely to the predictions of the Nichols and Mullins model.

The preceding experimental studies and models have laid a successful framework for understanding the instability of two somewhat different cases: two-dimensional films, for which microstructure and an underlying substrate are important, and one-dimensional isotropic wires surrounded by an isotropic medium. In practice, metal nanowires could possess a combination of these characteristics; i.e., they could be anisotropic in their surface and bulk properties, and be in intimate contact with a substrate. Under these conditions, it is unlikely that either the thin film or free standing wire models could be applied directly.

Gurski and McFadden10 have addressed one of these complicating issues by modeling the capillary instability of a free standing rod with anisotropic surface properties. They concluded that both the magnitude and sign of the anisotropy were critical characteristics to consider. Powers and Glaeser11 have also experimentally demonstrated orientation dependent Rayleigh instability of sapphire rectangular channels, for which the “rod” was the open space inside a channel. McCallum et al.12 modeled isotropic lines adhered to a

[Electronic mail: hol206@lehigh.edu.]


103, 024315-1
substrate and found that the substrate had a stabilizing effect as compared to the original model of Nichols and Mullins. Karim et al.\textsuperscript{13} investigated the effect of the microstructure of Au nanowires on the breakdown behavior and found that single crystalline nanowires tend to have a larger spacing between the agglomerated beads. Srolovitz et al.\textsuperscript{14} have modeled the morphological evolution of lines on substrates, but which exhibit a “bamboo” microstructure. They showed that lines with grain size larger than a certain equilibrium grain size would pinch off into beads driven by minimization of surface energy.

In the work described by this paper, Cu nanowires of constant thickness but different widths were fabricated on a single crystal sapphire substrate and annealed. The morphological stability of these wires was studied and compared to the theoretical predictions. Sapphire was chosen as the substrate material because of its chemical inertness with Cu and high thermal stability. An elevated annealing temperature of 700 °C was selected to intentionally accelerate the breakdown process, which is presumably thermally activated. The experimental results are discussed in reference to corresponding values calculated from theoretical models in the literature.

II. EXPERIMENT

C-plane single crystal sapphire substrates (Saint-Gobain Crystals, 330 μm thick) were used in this study. The metal nanostructures were fabricated through conventional E-beam lithography (Model LEO 1550 VT). The stages in the fabrication process are depicted schematically in Fig. 1. In order to achieve an undercut structure for a clean lift-off, two layers of positive polymethyl methacrylate (PMMA) photoresist with different molecular weights (495K and 950K) were sequentially spin-coated on a sapphire substrate. To minimize any charging (and hence pattern distortion) due to the non-conducting sapphire substrate, all patterns were written in variable-pressure mode at a N$_2$ pressure of 30 Pa and an accelerating voltage of 30 kV. Cu films of thickness of ~100 nm were deposited on the sample using a resistance-heated thermal evaporator. The purity of the Cu source was 99.999%. The final lift-off was carried out by dissolving the remaining photoresist in acetone, followed by mild stirring/ agitation. Periodic arrays of lines with widths ranging from 110 to 300 nm were fabricated; in each case, the line to line spacing was approximately 1 μm. Along the wire length, individual lines were separated into two 120 μm long segments with a gap of 1 μm; this was done to facilitate the study of morphology changes at the ends of the lines during annealing.

After fabrication, the Cu nanostructures were subjected to a series of thermal treatments. Due to the low oxidation resistance of copper, annealing of the Cu line samples was carried out in dry nitrogen. This was achieved by reducing the atmosphere in the furnace tube to less than $10^{-4}$ Torr and purging several times with nitrogen to remove the residual oxygen. A pressure of 100 Torr was maintained during annealing with N$_2$ flow. As mentioned earlier, an elevated temperature of 700 °C was selected to ensure breakdown in a reasonable period of time. Two annealing times were employed: 5 and 60 min. Ramp-up to temperature was achieved in less than 2 min, whereas cooling down to room temperature usually took about half an hour.

The morphologies of the nanowires were characterized both before and after annealing using high resolution field emission scanning electron microscopy (FE-SEM, Hitachi S4300). The diameters of the agglomerated beads were determined from SEM images (taken at zero tilt) by measuring the longest and shortest lateral dimensions of each bead and taking the average value. In each case, the number of beads measured was greater than 50. The average bead separation was determined by counting the number of beads over a given length of 40 μm in ten different Cu wires. In order to characterize the microstructure of the as-deposited Cu films using a transmission electron microscope (TEM), samples at stage 4 in the fabrication process (see Fig. 1) were deliberately fabricated with insufficient photoresist undercut. As a
result, the metal lines were connected to the metal on top of the resist. During lift-off, therefore, it was possible to transfer the overlying metal film, along with the attached line structures, onto a TEM grid. To evaluate the Cu grain structure after heat treatment at 700 °C for 1 h, TEM cross-sectional samples of the annealed Cu wires were prepared by a focused ion beam (FIB) instrument (FEI Strata DB 235). Grain structures were examined using JEOL 2000 with operating voltage of 200 kV.

### III. RESULTS AND DISCUSSION

#### A. Line microstructure and morphology

The grain structures of the evaporated ~100 nm thick Cu films were studied by TEM with plan view samples. As can be seen from the bright field (BF) and dark field (DF) images in Figs. 2(a) and 2(b), the Cu films were polycrystalline, with no apparent epitaxial relationship to the single crystal substrate. TEM also confirmed that the microstructure of the Cu film overlying the PMMA was the same as that of the line structures on the sapphire substrate. The grain structure was duplex, with some grains as large as ~600 nm, interspersed with very small grains with dimensions less than 50 nm. The grain size distribution is shown in Fig. 3. It should be noted that grains with dimensions less than 50 nm were not counted. The average grain size for the 100 nm as-deposited Cu was found to be around 200 nm, which is approximately two times the film thickness and consistent with many prior studies. With regard to the grain structure of the annealed lines, a TEM micrograph of a longitudinal section of a 250 nm wide copper line after annealing for 1 h is shown in Fig. 4. It shows columnar grains with sizes all significantly larger than 100 nm, indicating that some grain growth had taken place.

None of the Cu nanowires, regardless of line width, underwent noticeable morphological change during annealing for 5 min at 700 °C (T/Tm = 0.72, Tm is the melting temperature). However, with the longer thermal treatment (1 h at temperature of 700 °C), wires with width equal to or less than 160 nm completely broke down into discrete, widely spaced beads [Figs. 5(a) and 5(b)]. Lines with widths between 200 and 300 nm also showed significant agglomeration, but breakdown was not complete [Figs. 5(c) and 5(d)].
ture, the equivalent radius ($r_e$) was determined for each set of nanowires, where $r_e$ is defined as the radius of a free standing cylindrical rod having the same cross-sectional area as the rectangular wires. As can be seen from Table I, on normalizing the measurements of bead diameter ($d$) and bead spacing ($\lambda_m$) to $r_e$, the results for the 110, 145, and 160 nm wires are in fairly close agreement, i.e., they are about 4.6 and 16 times the equivalent radius of the Cu wires, respectively. The volume of the Cu beads after breakdown is in reasonable agreement with the original wire volume ($1.47 \times 10^7$ nm$^3$ versus $1.57 \times 10^7$ nm$^3$), assuming the agglomerated beads are truncated spheres with a contact angle of 110°.

### B. Mechanism of line breakdown

The most likely mechanisms for the line breakdown are Rayleigh instability$^7$ or grain boundary grooving.$^7$ Either is plausible, given that the Cu lines have significant surface curvature, as well as a mostly columnar microstructure that develops during annealing. Grain boundary grooving is the generally accepted mechanism for polycrystalline thin film breakdown.$^7$ For lines on substrates, although a one-to-one relationship between bamboo structured grains and agglomerated beads has been assumed in models,$^{14}$ no such experimental relationship between the individual grain size and the spacing of agglomerated beads has been reported explicitly in the open literature. For lines of similar dimensions to those studied here, the model of Srolovitz and Thompson predicts that the critical grain size above which the lines will break into beads is less than 101 nm.$^{14}$ Since the average size of the larger grains in our Cu lines is $\sim 200$ nm, it is feasible that they could break down through grain boundary grooving according to the prediction of Srolovitz and Thompson. However, no simple correlation between the bead dimensions and grain size was observed. In contrast, for the line widths tested, the bead diameter was found to be a constant multiple of the equivalent radius. Furthermore, the spacing was several times larger than the average grain size, and also larger than the vast majority of grains. It is possible that only certain grain boundaries are eventually capable of grooving to the extent needed for breakdown, but it is unlikely that these special boundaries could be so regularly spaced as indicated by the $\lambda_m$ parameter. Although grain boundary grooving cannot be discounted completely, it is believed that Rayleigh instability induced by surface curvature is the more likely cause of the morphology changes. Note that the process of breakdown due to Rayleigh instability does not depend on the grain size; for example, Toimil Molares$^2$ et al. reported that their free standing Cu nanowires which underwent breakdown were single crystalline.

### C. Transport mechanisms

The observed changes in nanowire morphology could take place via several possible transport mechanisms, i.e., volume diffusion, surface diffusion, and evaporation-condensation. The contribution of each mechanism to the overall transport can be estimated from the values for the volume diffusion parameter $A(T)$, the surface diffusion parameter $B(T)$, and the evaporation-condensation parameter $C(T)$, where

\[
V\text{olume diffusion parameter: } A(T) = \frac{\gamma d \Omega D_v(T)}{kT},
\]

Note that all length values are given in units of nm.

#### TABLE I. Comparison of values of bead size ($d$) and spacing ($\lambda_m$) between experimental results (present study) and theoretical predictions from the literature. The wire heat-treatment was 1 h at 700 °C in nitrogen.

<table>
<thead>
<tr>
<th>Wire Widths</th>
<th>Experimental results</th>
<th>Theoretical calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lines on a substrate</td>
<td>$d$</td>
<td>$\lambda_m$</td>
</tr>
<tr>
<td>110</td>
<td>266 ± 32</td>
<td>910 ± 38</td>
</tr>
<tr>
<td>(4.48(r_e))</td>
<td>(15.3 ± 0.6(r_e))</td>
<td>(3.78(r_e))</td>
</tr>
<tr>
<td>145</td>
<td>318 ± 31</td>
<td>1031 ± 59</td>
</tr>
<tr>
<td>(4.69(r_e))</td>
<td>(15.2 ± 0.9(r_e))</td>
<td>(3.78(r_e))</td>
</tr>
<tr>
<td>160</td>
<td>331 ± 28</td>
<td>1193 ± 110</td>
</tr>
<tr>
<td>(4.63(r_e))</td>
<td>(16.7 ± 1.5(r_e))</td>
<td>(3.78(r_e))</td>
</tr>
</tbody>
</table>

$^a$Reference 9.

$^b$Reference 12.
Surface diffusion parameter: \( B(T) = \frac{D_s(T) \gamma \Omega^2 \nu}{kT} \). (2)

Evaporation-condensation parameter:
\[
C(T) = \frac{\rho_0 \gamma \Omega^2}{(2\pi m)^{1/2}(kT)^{3/2}}.
\] (3)

In addition, the following dimensionless ratios \( \sigma_1 \) and \( \sigma_2 \), the corresponding ratio for the rate of surface diffusion versus evaporation-condensation, are defined according to the discussions in Ref. 9. The expressions for these quantities are as follows:

\[
\sigma_1 = \frac{B}{Ar},
\] (4)

\[
\sigma_2 = 0.38 \frac{B^{1/2}}{C} r^{-1/2}.
\] (5)

For the above equations, the symbols are defined in Table II. Values for \( A(T) \), \( B(T) \), \( C(T) \), \( \sigma_1 \), and \( \sigma_2 \) were calculated for Cu heat treated for 1 h at 700 °C. These are given in Table II, together with the values utilized for the various input parameters. Given that for the relevant heat-treatment conditions the value of the surface diffusion versus volume diffusion ratio (\( \sigma_1 \)) is about 200, it is reasonable to assume that the contribution from volume diffusion is negligible. Similarly, transport through evaporation is also negligible compared to surface diffusion.

### D. Driving force for line breakdown

In most cases, the breakdown of thin films or wires is driven by strain energy and/or surface energy. There is no source of strain energy for free standing rods, but for rods embedded in a solid matrix, the strain energy contribution can be large.\(^{20}\) As for certain films on substrates, surface energy can dominate; for example, Danielson et al.\(^{21}\) showed that for a 10 nm Si thin film on SiO\(_2\), the reduction of surface energy was the predominant driving force. However, for Cu deposited on sapphire, there are intrinsic and extrinsic stresses that are likely to exist due to growth conditions and differences of thermal expansion.\(^{22}\) In the following, we estimate the magnitudes of the total change in strain energy and surface energy for the Cu nanowires on annealing. For the surface energy calculations, segments of the metal wires with rectangular cross section were assumed to break down into individual truncated spheres of the same volume. The extent of truncation was set by the choice of the equilibrium contact angle for Cu on sapphire. Though the contact angle (\( \theta \)) of liquid Cu on sapphire has been reported to be 110° (nonwetting),\(^{23}\) all the samples in this study showed a much greater tendency to wet, presumably because the Cu is still in the solid state. Accordingly, a value of \( \theta = 70° \), which was obtained by measurements from cross section SEM images of the agglomerated Cu beads, was used in all the calculations. The surface free energy of Al\(_2\)O\(_3\) (\( \gamma_{\text{Al}_2\text{O}_3} \)) was calculated using the relationship given by Levi and Kaplan.\(^{24}\) The value for the average surface free energy of solid copper (\( \gamma_{\text{Cu}} \)) was taken as 1.52 J/m\(^2\).\(^{18}\) The interfacial energy between copper and sapphire (\( \gamma_{\text{Cu-Al}_2\text{O}_3} \)) was calculated through Young’s equation, where \( \gamma_{\text{Cu-Al}_2\text{O}_3} = \gamma_{\text{Al}_2\text{O}_3} - \gamma_{\text{Cu}} \cos \theta \).

With regard to the strain energy, it was assumed that any stress in the as-deposited nanowires was totally relaxed after breaking down into droplets. The stress evolution of Cu films on sapphire has been studied by Dehm et al.,\(^{22}\) and for the annealing temperature used in our study the lines should be in compression. In order to gain an understanding of the maximum contribution due to strain energy relaxation, an upper limit value of 200 MPa was assumed.

The change in strain energy and surface energy after annealing was calculated as a function of line width (see

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Values</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_s ) (cm(^2)/s)</td>
<td>Surface self-diffusion coefficient</td>
<td>( 4.76 \times 10^{-7} )</td>
<td>Ref. 16</td>
</tr>
<tr>
<td>( D_v ) (cm(^2)/s)</td>
<td>Volume (or lattice) diffusion coefficient</td>
<td>( 5.30 \times 10^{-12} )</td>
<td>Ref. 17</td>
</tr>
<tr>
<td>( \gamma_s ) (J/m(^2))</td>
<td>Surface free energy</td>
<td>1.52</td>
<td>Ref. 18</td>
</tr>
<tr>
<td>( \Omega ) (cm(^3)/atom)</td>
<td>Atomic volume</td>
<td>( 1.18 \times 10^{-23} )</td>
<td></td>
</tr>
<tr>
<td>( \nu ) (atoms/cm(^2))</td>
<td>No. of diffusing atoms/unit surface area</td>
<td>( 1.93 \times 10^{15} )</td>
<td></td>
</tr>
<tr>
<td>( r ) (cm)</td>
<td>Diffusion distance (equivalent radius)</td>
<td>( 1.0 \times 10^{-5} )</td>
<td></td>
</tr>
<tr>
<td>( k ) (J/K)</td>
<td>Boltzmann’s constant</td>
<td>( 1.38 \times 10^{-23} )</td>
<td></td>
</tr>
<tr>
<td>( P_0 ) (Pa)</td>
<td>Equilibrium vapor pressure of metal</td>
<td>( 3.81 \times 10^{-7} )</td>
<td>Ref. 19</td>
</tr>
<tr>
<td>( m ) (kg/atom)</td>
<td>Molecular weight</td>
<td>( 1.06 \times 10^{-25} )</td>
<td></td>
</tr>
<tr>
<td>( T ) (K)</td>
<td>Temperature</td>
<td>973</td>
<td></td>
</tr>
<tr>
<td>( t ) (s)</td>
<td>Thermal treatment time</td>
<td>3600</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Input parameters</th>
<th>Calculated transport parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A(T) ) (cm(^2)/s)</td>
<td>Volume diffusion parameter</td>
</tr>
<tr>
<td>( B(T) ) (cm(^2)/s)</td>
<td>Surface diffusion parameter</td>
</tr>
<tr>
<td>( C(T) ) (cm(^2)/s)</td>
<td>Evaporation-condensation parameter</td>
</tr>
<tr>
<td>( \sigma_1 )</td>
<td>Surface diffusion vs volume diffusion ratio</td>
</tr>
<tr>
<td>( \sigma_2 )</td>
<td>Surface diffusion vs evaporation-condensation ratio</td>
</tr>
</tbody>
</table>
In each case, the bead spacing was taken to be 16 times equivalent radius $r_e$, a value which was based on the experimental observations. The details of the calculations are given in the Appendix. It can be seen that per unit volume, the magnitude of the surface energy reduction is several orders of magnitude greater than the reduction in strain energy, hence the former is the dominant driving force for the morphological instability, and the strain energy contribution can be safely ignored. It is also clear from Fig. 6 that finer wires experience a larger driving force for surface energy minimization, which was substantiated by our experimental results. Note that the calculations are relatively insensitive to the value of the contact angle chosen, so that the use of $\theta = 110^\circ$ only resulted in a minor change in the total surface energy reduction, and the overall trend was not affected.

The curves in Fig. 6 were calculated assuming a bead separation of $16r_e$, which was the experimentally observed value. It is also possible to calculate the reduction in surface energy per unit volume for different values of bead spacing, and these results are shown in Fig. 7. The value of $\lambda_m = 8.89$ was selected because this is the prediction of the Nichols and Mullins model for a free standing rod. Note that there is a disparity in the appearance of the graphs in Fig. 7 compared to Fig. 6 because a log scale was used for the coordinate in Fig. 6. It can be seen that as the ratio $\lambda_m/r_e$ decreases, the curves are displaced to lower values of energy reduction. Significantly, for $\lambda_m/r_e = 8.89$, there is a critical line width ($\sim 85$ nm) above which breakdown due to surface energy considerations is not energetically favorable. Another way of interpreting Fig. 7 is that for a given starting line width, the driving force from surface energy reduction increases with increasing bead separation.

**E. Influence of substrate and kinetic considerations**

As described earlier, for the present study the breakdown of the Cu nanowires resulted in beads with a separation of $\sim 16r_e$. In contrast, for breakdown of free standing rods by surface diffusion, the Nichols and Mullins model predicts $\lambda = 8.89r_e$. The effect of having a substrate present was analyzed by McCallum et al. They modeled lines with cross sections corresponding to truncated spheres and showed that the substrate has a stabilizing effect on breakdown and that the degree of stabilization is dependent on the contact angle. Even for a contact angle of $180^\circ$, the value of $\lambda_m$ was calculated to be $\sim 10.5r_e$. This is larger than the Nichols and Mullins value of $8.89r_e$, indicating that even a single line of contact with the substrate stabilizes cylindrical rods. If the prediction of the McCallum model is computed using $\theta = 70^\circ$, we obtain the wavelength of maximum instability $\lambda_m$ to be $14.2r_e$, which is close to the present experimental measurements of $16r_e$. The experimental results, therefore, are consistent with the idea that the substrate modulates the degree of morphological change. Although the agreement between the McCallum model and our experiments is quite reasonable, it should be noted that using the published Cu/sapphire contact angle of $110^\circ$ results in a greater disparity between the values, i.e., $11.4r_e$ versus $16r_e$. In addition, Cu nanowires in the present studies are polycrystalline, with no apparent epitaxial relationship to the substrate, therefore the same results would be expected even if the substrate were polycrystalline.

Nichols and Mullins also studied the kinetics of surface energy driven shape changes of free standing cylindrical rods. As might be expected, there is strong temperature dependence. Further, the time required to achieve a given degree of breakdown was predicted to scale with $r^4$, where $r$ is the rod radius. Although the kinetics of the nanowire breakdown was not the focus of the present study, nonetheless we can make the following observation by substituting...
the appropriate values into the Nichols and Mullins analysis (see Appendix), the prediction is that the breakdown of 110 nm wires should occur in only 6 s. With the McCallum et al. model of lines on a substrate,\textsuperscript{12} for a 110 nm Cu wire and a 70° contact angle the predicted breakdown time was $\sim 25$ s. Although in the present work the breakdown times for the 110, 145, and 160 nm width Cu wires were not measured specifically, it is known that they exceeded 300 s because after this length of heat-treatment the wires were still intact. This time discrepancy is consistent with the greater stabilization effect demonstrated by the observed bead spacing. Clearly much more work is necessary, but the present results suggest that the models in the literature underestimate the stabilizing effects and overestimate the rate of breakdown. Whether this can be attributed to inaccuracies in the values of the diffusion parameters utilized, or some unknown aspect of the stabilizing effect of the substrate and/or surface films, remains to be determined.

IV. SUMMARY

The morphological stability of Cu nanowires on a (0001) sapphire substrate was studied as a function of wire width in the range 110–300 nm. For annealing treatments in nitrogen at 700 °C, it was found that the wires were stable after annealing for 5 min. However, for heat-treatments of 1 h duration, lines of width 160 nm (or less) broke down into discrete, separated beads. Based on considerations of the Cu microstructure and the bead spacing, it was inferred that Rayleigh instability, rather than grain boundary grooving, was the mechanism of breakdown. Calculated values of transport parameters suggested that surface diffusion was the predominant transport mechanism. The experimentally observed values of bead spacing were larger than those predicted by the Nichols and Mullins model for free standing rods, but showed good agreement with a theoretical treatment that took into account the stabilizing influence of the substrate. Using bead separation distances and Cu-sapphire contact angles derived from experiment, it was shown that on breakdown, the energy savings due to reduction in surface energy is many orders of magnitude greater than that associated with strain energy reduction. It was also shown that as the assumed bead separation (normalized with respect to the effective radius) decreases, breakdown into closely spaced beads may be energetically unfavorable for lines greater than a critical width.

ACKNOWLEDGMENTS

Financial support from the National Science Foundation (Grant No. DMR- 211078) as well as the Army Research Laboratory (Cooperative Agreement No. 11NF-04-2-0015) is gratefully acknowledged. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Office, Army Research Laboratory, or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon.

APPENDIX: CALCULATION DETAILS

1. Changes in surface and strain energy on wire breakdown

a. Calculation of change in surface energy on line breakdown

For the rectangular cross-section wires, we define the equivalent radius ($r_e$) as the radius of a circle having the same cross-section area, where

$$ r_e = \sqrt{\frac{WH}{\pi}} \quad (A1) $$

and $W$ and $H$ are the original width and height of the lines, respectively.

From experiment, the bead spacing ($\lambda_m$) was about 16 $r_e$, therefore the volume of the segment of wire ($V_o$) which undergoes agglomeration is given by

$$ V_o = \lambda_m WH = 16\pi r_e^3. \quad (A2) $$

For a truncated sphere with dimensions as shown in Fig. 8, for $\theta = 90$,

$$ r = R \sin \theta, \quad (A3a) $$

$$ h = R - R \cos \theta = R(1 - \cos \theta). \quad (A3b) $$

Then the volume ($V_{\text{sphere}}$) of the truncated sphere above the surface of the substrate is given by

$$ V_{\text{sphere}} = \frac{\pi}{6} h(3r^2 + h^2). \quad (A4) $$

Substituting in values for $r$ and $h$ from Eqs. (A3a) and (A3b), respectively, we obtain

$$ V_{\text{sphere}} = A'R^3, \quad (A5) $$

where

$$ A' = \frac{\pi}{6}(1 - \cos \theta)[3 \sin^2 \theta + (1 - \cos \theta)^2]. \quad (A6) $$

From conservation of volume considerations, we can equate expressions for $V_o$ [Eq. (A2)] to $V_{\text{sphere}}$ [Eq. (A5)] and rearrange to obtain the following expression for $R$, the radius of the truncated sphere:
\[ R = r_e \left( \frac{16\pi}{A^2} \right)^{1/3}. \]  

The base area of the truncated sphere \( S_{\text{base}} \) is given by \( \pi r^2 \). Substituting for \( R \) in terms of \( R \) [Eq. (A3a)] and \( r_e \) [Eq. (A7)] gives

\[ S_{\text{base}} = B' r_e^2, \]  

where

\[ B' = \pi \left( \frac{16\pi}{A^2} \right)^{2/3} \sin^2 \theta. \]  

The total surface energy of the wire segment (length \( \lambda_m \)) before breakdown, \( E_{\text{r-before}} \), is

\[ E_{\text{r-before}} = (2H\lambda_m + W\lambda_m) \gamma_{\text{Cu}} + W\lambda_m \gamma_{\text{Cu-Al}_2\text{O}_3}, \]  

where \( \gamma_{\text{Cu}} \) is the surface energy value for copper, and \( \gamma_{\text{Cu-Al}_2\text{O}_3} \) is the Cu-sapphire interfacial energy.

The total surface energy of the beads after breakdown, \( E_{\text{r-after}} \), is given by

\[ E_{\text{r-after}} = S_{\text{cap}} \gamma_{\text{Cu}} + S_{\text{base}} \gamma_{\text{Cu-Al}_2\text{O}_3} + (W\lambda_m - S_{\text{base}}) \gamma_{\text{Al}_2\text{O}_3}, \]  

where \( \gamma_{\text{Al}_2\text{O}_3} \) is the surface energy of sapphire. Therefore, the change in surface energy \( \Delta E_s \) for the line segment is

\[ \Delta E_s = E_{\text{r-after}} - E_{\text{r-before}}. \]  

Substituting expressions for \( S_{\text{base}} \) [Eq. (A8)] and \( S_{\text{cap}} \) [Eq. (A11)] yields

\[ \Delta E_s = \gamma_{\text{Cu}} C' r_e^2 - 16 r_e \left( 2H + W \right) + \gamma_{\text{Cu-Al}_2\text{O}_3} \left( B' r_e^2 - 16 W r_e - B' r_e^2 \right). \]  

Using this expression, the value of \( \Delta E_s \), normalized per unit volume, was plotted as a function of wire width, for a bead separation of \( 16 r_e \) (Fig. 6). In Fig. 7, the corresponding quantity is plotted as a function of the line width, but for different values of \( \lambda_m \), namely \( 16 r_e \) and \( 8.89 r_e \).

### b. Calculation of change in strain energy on line breakdown

Assuming that the strain energy is relaxed completely on breakdown, the total change in strain energy \( \Delta E_{\text{strain}} \) (per unit volume) is equal to the initial strain energy in the wires (per unit volume), that is,

\[ \Delta E_{\text{strain}} = \frac{(1 - \nu) \sigma^2}{E}, \]  

where \( E \) is Young’s modulus, \( \nu \) is the Poisson’s ratio of Cu, and \( \sigma \) is the stress of the Cu wire. In the present work, the values of \( \nu \) and \( E \) for copper were taken as 0.34 and 130 GPa, respectively, and the value of the (compressive) stress was assumed to be 200 MPa. Using Eq. (A17), the value of \( \Delta E_{\text{strain}} \) was plotted as a function of wire width, for a bead separation of \( 16 r_e \) (Fig. 6).

### 2. Breakdown kinetics of nanowires

For a free standing rod Nichols and Mullins\(^ {16} \) define a dimensionless parameter \( \tau \) as

\[ \tau = \frac{B(T) t}{l^2}, \]  

where \( B(T) \) is the surface diffusion parameter, \( t \) is time, and \( l \) is the rod size parameter, which is in turn given by \( (\pi/16)r \) (where \( r \) is the radius of the cylindrical rod). They subsequently show that for a nontapered rod, the value of \( \tau \) for complete breakdown is 4415. Substituting the appropriate value for \( B(T) \), the model predicts a breakdown time of \( 6 \) s for Cu wires of cross section \( 110 \times 100 \) nm\(^2 \).

For the model by McCallum \textit{et al.},\(^ {12} \) the maximum growth rate \( q_m \) is defined as

\[ q_m = q_m \left( \frac{B(T)}{r_e^2} \right), \]  

where \( q_m \) is the maximum nondimensional growth rate, and \( B(T) \) and \( r_e \) are defined as previously. Based on McCallum \textit{et al.}’s graphical solution for \( q_m \) as a function of the contact angle \( \theta \), and using the experimentally observed value of \( \theta \sim 70^\circ \), the value of the maximum nondimensional growth rate was estimated to be 0.037. For the 110 nm width lines, substituting the appropriate values for \( B(T) (1.33 \times 10^{-21} \text{ cm}^4/\text{s}) \) and \( r_e (59.3 \) nm) gives the maximum growth rate of the instability, \( q_m \sim 0.04 \) s\(^{-1} \), and the resulting characteristic time for the growth of instability as \( \sim 25 \) s.