Comparison of the agglomeration behavior of Au and Cu films sputter deposited on silicon dioxide

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The agglomeration behavior of Cu and Au films each with a thickness of 5 and 50 nm, deposited on thermally grown SiO\textsubscript{2} by dc magnetron sputtering, was investigated with scanning electron microscopy. The size of Cu islands formed by agglomeration increased with increasing annealing temperature. Also, the agglomeration of Cu films seem to follow the grain boundary grooving process. On the other hand, Au islands have an identical size at different annealing temperatures. Au films were observed to agglomerate via nucleation of voids followed by the fractal growth of voids. The fractal dimension was determined to be 1.7 indicating that the fractal growth of voids can be described with a diffusion limited aggregation model. Finally, the kinetics of agglomeration of the Au films was described with an Avrami-type equation. © 2003 American Institute of Physics. [DOI: 10.1063/1.1556178]

I. INTRODUCTION

Agglomeration of a thin film resulting from solid state dewetting is an isolated island formation process from a continuous film. It is a thermally activated process reducing the free energy of the system by rearranging the film surface, the interface between the film and substrate, and the grain boundaries within the film. Without elastic strain, Young’s relationship should be satisfied for an island in equilibrium on a planar substrate:

\[ \gamma_i + \gamma_m \cos \theta = \gamma_{SiO_2}, \]  

(1)

where \( \theta \) is the contact angle, \( \gamma_i \) is interface energy between the film and substrate, \( \gamma_m \) and \( \gamma_{SiO_2} \) are the surface energies of the metal film and the SiO\textsubscript{2} substrate, respectively (see Fig. 1). From a thermodynamic point of view, a giant single island has the least free energy for the system. In reality, however, small islands are formed; further coalescence is slow unless the temperature is high enough. Therefore, it is important to understand the agglomeration sequences, also called kinetic paths, because they determine the size and distribution of islands during the agglomeration of the thin film.

The agglomeration mechanism generally reported is the “grain boundary grooving” mechanism.\textsuperscript{1-5} According to this mechanism, grooves are first formed through the force balance at the triple junctions found where a grain boundary of the film meets either the film surface or the interface between the film and the substrate. As a result, parts of the substrate surface are exposed and a film finally agglomerates. In this work, we propose another agglomeration mechanism to explain the agglomeration of Au films sputter deposited on the SiO\textsubscript{2} substrate. Au films were observed to agglomerate through the nucleation of voids and the subsequent fractal growth of the voids as opposed to the “grain boundary grooving” mechanism. Jiran and Thompson\textsuperscript{6} reported void nucleation in agglomeration of Au films which they thought was due to grain boundary grooving even though the spatial density of grain boundaries is much higher than that of the voids. Also, Hummel \textit{et al.}\textsuperscript{7} earlier suggested that agglomeration of Au film is due to grain boundary grooving without detailed observation of the void growth. In this work, we also studied the agglomeration of Cu films as well as Au films, and compared grain boundary grooving and void nucleation and subsequent fractal growth processes.

II. EXPERIMENT

First, we deposited both Au and Cu films with a thickness of 5 nm on a thermally grown 100 nm thick SiO\textsubscript{2} substrate using dc magnetron sputtering. The base pressure for sputtering was \( 5 \times 10^{-6} \) Torr and the operating pressure was 4 mTorr. The sputtering rates were set to about 30 nm/min for both films. The microstructure of the sputter-deposited Cu film was previously confirmed to be a columnar structure by cross-sectional transmission electron microscopy (TEM).\textsuperscript{8} On the other hand, that of the Au film was not analyzed due to the difficulties in TEM sample preparation resulting from the poor adhesion of the Au film on a SiO\textsubscript{2} substrate. Au films were annealed in a hydrogen environment in a quartz tube furnace at 300 °C for 15, 30, and 60 min. In addition, both Au and Cu films were annealed for 15 min at 300, 500, 700, and 900 °C in a hydrogen environment in order to investigate the effect of annealing temperature on the agglomeration process. The volume fraction of impurities (including oxygen) in the annealing environment was below \( 10^{-7} \) atm.

Since the 5 nm thick films were found to agglomerate too fast to record the detailed sequence of the agglomeration process, we also prepared 50 nm thick films to observe the
sequence of agglomeration. The 50 nm thick Au films were then annealed in either a hydrogen or nitrogen environment at 700 °C and Cu films were annealed only in a hydrogen environment at 300 °C by varying the annealing time. The agglomeration of Cu films was not observed in a nitrogen environment due to the copper oxide formation at the surface of the Cu films. Preliminary experiments have shown that although the annealing temperature varies from 300 to 625 °C for the Cu film and from 500 to 700 °C for the Au film, the agglomeration sequences did not change significantly. Only the kinetics of agglomeration becomes faster when the annealing temperature increases. Also, the kinetics of agglomeration between Au and Cu is found to be quite different even though the melting temperature of these metals are nearly same. This is thought to be due to the different agglomeration sequences for the Au and Cu films. Therefore, for the precise observation of agglomeration sequences, it is thought to be experimentally more effective to observe at different temperature than at a fixed temperature. Therefore, we annealed the Au and Cu films at different annealing temperatures in order to finish the agglomeration process within 3 h in each system. The surface morphologies of the films before and after annealing were analyzed with a scanning electron microscope (SEM).

III. RESULTS

A. Variation of the annealing time of 5 nm thick films

Figure 2 shows the surface morphologies of 5 nm thick Au films before and after annealing at 300 °C for 15, 30, and 60 min. It is clear that the Au films were fully agglomerated after annealing for only 15 min. The size and density of Au islands is illustrated in Fig. 3. It demonstrates that the average size and density of Au islands are about 110 nm and 30/μm², respectively, after annealing for 15 min. Also, they are not significantly changed with a further increase of annealing time. This indicates that Au islands once formed within 15 min at an annealing temperature of 300 °C do not coalesce.

B. Variation of the annealing temperature of 5 nm thick films

The surface morphologies of 5 nm thick Au films and Cu films after annealing in a hydrogen environment are presented in Figs. 4 and 5, respectively. The annealing tempera-
ture was varied from 300 to 700 °C and the annealing time was fixed at 15 min. Also, Fig. 6 illustrates the size and the spatial density of the Au and Cu islands as a function of annealing temperature. It is clear from this that Au islands were formed with a size and density of about 95 nm and 10/μm², independent of the temperature. On the other hand, the size of the Cu islands increased from 40 to 55 nm and the density decreased from about 220 to about 60/μm² with the increase of temperature from 300 to 700 °C showing the temperature dependence of the agglomeration of Cu films.

C. Observation of the sequence of agglomeration with 50 nm thick films

1. Au/SiO₂ system

Figure 7 displays the surface morphologies of the 50 nm thick Au films annealed at 700 °C in a hydrogen environment. It is found that the voids are formed on the substrate at the initial stage of agglomeration [Fig. 7(a)]. The voids then grow into an irregular shape with a branched structure forming at the edge of each shape [Fig. 7(b)]. With further annealing time, the size of branches (a fractal) increases [Fig. 7(c)]. The fractals coalesce with further annealing [Fig. 7(d)] to cover the whole film [Figs. 7(e)–7(f)]. Agglomeration of the Au film annealed in a nitrogen environment was found to follow a similar sequence to that found in a hydrogen environment. The white bumps shown on the nonagglomerated surface [marked with arrows in Fig. 7(b)] are thought to be Ar gas bubbles formed from Ar gas elements incorporated in the film during the sputtering deposition process. These bubbles were not observed in the e-beam evaporated Au films deposited on SiO₂. However, the agglomeration sequence of the Au film deposited by evaporation was similar to that of the sputtered films, suggesting that the agglomeration sequences were not affected by the formation of bubbles.

We have analyzed the number density of fractals as a function of annealing time, as illustrated in Fig. 8. It is interesting to note that most fractals were generated during the first 30 min and after that they continued to grow but with no more fractals being generated. Thus, the overall agglomeration process takes place in two distinct stages: the nucleation of voids followed by the growth of these voids as fractals. In order to analyze the fractal growth rate, each fractal is represented in a simplified manner as a disk, as shown schematically in Fig. 9. The average size of fractals is then plotted as a function of annealing time. As shown in Fig. 10, the fractal diameter increases linearly with the annealing time. The growth rate of fractals formed in a hydrogen environment is slightly larger than the growth rate in a nitrogen environment.

2. Cu/SiO₂ system

The agglomeration sequence of Cu films was also studied for a comparison with that of the Au films. Figure 11 shows the agglomeration sequence of Cu films annealed at 300 °C in a hydrogen environment. It should be noted that the Cu films were annealed at a lower temperature (300 °C)
than that of the Au films (700 °C) in order to investigate the agglomeration sequences on a similar time scale (120 min). In contrast to the agglomeration behavior of the Au films, the Cu films seemed to agglomerate by following the typical grain boundary grooving behavior, in which holes first form at the grain boundary grooves and then grow through the grain boundaries. No fractal growth of a hole was observed in the Cu films. Also, since the agglomeration sequence did not change significantly when the volume fraction of impurity was reduced from $10^{-7}$ to $10^{-10}$ atm, it is thought that the partial pressure of oxygen is not the main variable determining the agglomeration of the Cu and Au films.

IV. DISCUSSION

In Sec. III, we demonstrated that there are quite different agglomeration behaviors for the Cu and Au films when both have a thickness of 50 nm. First, the agglomeration of Cu films take place according to the grain boundary grooving sequence. Voids nucleate at some of the grain boundary triple junctions where the grooves are deeper and then grow through surface diffusion. Most Cu agglomerates are contiguous with some isolated hillocks occurring. In contrast to the agglomeration of the Cu films, the Au films have fractals at certain sites with a distance of 50–60 μm between the fractal centers independent of either the grain sizes or the distances between grain boundary grooves, as shown in Fig. 7(b). The distance between voids is much larger than the average grain size by factors of $10^2$–$10^3$, which undermines void formation at grain boundary grooves. Voids then spread in a branching fashion until they impinge upon others [see Fig. 7(d)]. The final morphology of the Au films after void branches have covered the whole substrate is quite similar to that for the Cu films. However, Au agglomerates have a much thornier shape with sharper edges than the Cu agglomerates. We have considered the overall agglomeration to be a two stages process: void nucleation followed by their growth as fractals.

A. Voids nucleation

A thin film deposited by sputtering has a vacancy concentration much higher than the equilibrium concentration at the annealing temperature. Therefore, void nucleation observed in the 50 nm thick Au films is hypothesized to be due to supersaturated excess vacancies. Figure 12 presents schematic diagrams for an as-deposited film containing excess vacancies and a void nucleus formed at the interface between the Au and SiO$_2$. From heterogeneous nucleation theory, the critical free energy for the formation of a nucleus in the form of a spherical cap is given by

$$\Delta G^* = 16\pi \gamma^3_{\text{Au}} S(\theta)/(3\Delta G_V^2),$$

(2)

where $\Delta G_V$ is the volume free energy change by the condensation of excess vacancies in a void nucleus and $S(\theta)$ is equal to

$$S(\theta) = (2 - \cos \theta)(1 + \cos \theta)^2/4,$$

(3)

where $\cos \theta = (\gamma_{\text{SiO}_2}/\gamma_i)/\gamma_{\text{Au}}$. For example, if we calculate with a typical limiting value for observable nucleation of $\Delta G^* = 60kT$, $\theta = 140^\circ$, and $\gamma_{\text{Au}} = 1537$ mJ/m$^2$, then $\Delta G_V V^*$ required for a nucleus of volume $V^*$ becomes about $9.3 \times 10^{-17}$ J at $T = 300$ °C. The void nucleus corresponds to a cluster of 23–24 vacancies. From diffusion data, the enthalpy for an Au vacancy is about 0.9 eV or $1.44 \times 10^{-19}$ J.
Thus, if the entire enthalpies associated with 24 excess vacancies become the driving force, void nucleation at the Au/SiO\textsubscript{2} interface becomes possible.

It is a simple matter to identify the location of void nucleation sites. Possibly, the boundary triple junctions at SiO\textsubscript{2} interfaces may be one of the nucleation sites. Besides, there are many other potential sites such as Ar gas bubble sites or any other sites of high stress due to the difference in the thermal expansion coefficient between Au\textsuperscript{15} and SiO\textsubscript{2}\textsuperscript{16}. Void nucleation by stress buildup could be more plausible in the Au films rather than in the Cu films due to the possibility of Cu oxides forming within the SiO\textsubscript{2} substrate as a buffer layer. In a printed circuit board fabrication process involving silane, it is known that Cu tends to form an oxide layer through Si–O–Cu bonding. Likewise, the Cu atoms in contact with SiO\textsubscript{2} or with oxygen in the vacuum chamber could form oxides. In fact, void nucleation can be explained in terms of a stress relief process. Basically, the void nucleation via clustering of excess vacancies may also occur in Cu films. However, the experimental results show that void for-
FIG. 10. Growth rate of fractals in Au system before coalescence of fractals occurs. Annealing temperature is 700 °C.

FIG. 11. SEM images of Cu films annealed in hydrogen environment at 300 °C for (a) as-deposited, (b) 10 min, (c) 20 min, (d) 40 min, (e) 60 min, and (f) 120 min.

FIG. 12. Schematic diagram of void nucleation at the interface between Au and SiO₂: (a) as-deposited film containing excess vacancies and (b) void nucleation.
mation through grain boundary grooving seems dominant since it occurs at a higher rate. Without doubt, more investigations are needed on why the grain boundary grooving mechanism is active in Cu but not in Au, for example, information on impurity segregation at a grain boundary and a surface should be useful as the depth of a groove is affected by segregation.

B. Void growth

Upon nucleation, a void grows as Au atoms diffuse away while vacancies diffuse into the void in order to lower the free energy of the system. Eventually, the void would perforate the Au film, creating a puncture. The puncture then expands laterally, creating a potbellied rim through Au surface diffusion. Next the potbellied rim becomes subject to some surface perturbations or instabilities such as Rayleigh instability, which may create void branches. Each branch then acts just like the initial puncture, creating a new set of branches. Branch groups keep growing until they impinge on each other. Though they seem to have no effect on void nucleation, grain boundaries should exert some influence on the paths of void branches. In Fig. 13, the right side displays SEM pictures for Au agglomerates advancing radially from a void nucleation site. A close examination reveals bright images at the edges of the Au agglomerates, indicating steep ridges.

Upon further annealing, banks between branches become narrower with accumulation of Au atoms occurring. When banks make an equilibrium contact angle with the SiO₂ substrate, they become stable as illustrated in Fig. 14. As a result, the minimum branch spacing and the island size are determined. It is thought that the identical size of the islands shown in Fig. 6 is attributed to the fact that the identical branch spacing is independent of temperature.

We simulated the agglomeration behavior of Au films with a diffusion limited aggregation (DLA) model, shown in the left column of Fig. 13, and compared to the SEM images. DLA mimics a fractal growth process with the assumption that a particle moves randomly until it encounters either the seed or other particles. The similarity between the DLA simulation and the SEM images suggests chaotic agglomeration kinetics but with some self-assembling features. Figure 15 presents the fractal dimension of Au fractals (a) annealed at 700 °C in a hydrogen environment for 90 min and (b) in a nitrogen environment for 120 min.

FIG. 15. Fractal dimension of Au films annealed at 700 °C (a) in a hydrogen environment for 90 min and (b) in a nitrogen environment for 120 min.

FIG. 14. Schematic growth morphology of void branches.

FIG. 13. Comparison of DLA simulation results (left column) and experimental results of agglomeration of Au film (right column).
annealed both in a hydrogen and in a nitrogen environment. A box-counting method\textsuperscript{19} yields a fractal dimension of about 1.7 for both environments, supporting the applicability of the DLA model to the agglomeration of Au films.

For simplicity, the shape of a fractal was assumed to be a disk (see Fig. 9). In a film of volume \( V \), the change in the agglomerated volume of one fractal during an annealing time \( dt \) is then given by

\[
dV_a = \pi d_f^2 \left( R + dR - R \right)^2 = 2 \pi d_f R dR = 2 \pi d_f V_f^2 dt,
\]

where \( V_f \) is the volume of a fractal, \( d_f \) is the film thickness, \( R \) is the radius of a fractal, \( t \) is the annealing time, and \( V_f \) is the growth rate of the fractal. With a constant \( \nu_g \), \( R = \nu_g t \).

The total change in the volume of the agglomerated region, \( dV_a \), is proportional to \( \rho dV_f \), where \( \rho \) is the density of fractals. Only the untransformed region contributes to the nucleation and growth of new fractals. Thus \( dV_a \) is equal to

\[
dV_a = \rho (V - V_a) dV_f = 2 \pi \rho d_f \nu_g^2 (V - V_a) dt.
\]

Upon integrating Eq. (5) with respect to time starting at \( t_0 \), the time taken before nucleation occurs, the volume fraction of agglomeration \( f(= V_a/V) \) becomes

\[
f = 1 - \exp \left[ - \pi \rho d_f \nu_g (t - t_0)^2 \right].
\]

This is the well-known Avrami equation\textsuperscript{21}, which describes the fraction of agglomeration as a function of annealing time. As shown in Fig. 16, the experimentally measured agglomeration fractions of Au films annealed in both a hydrogen and a nitrogen environment correspond well to the typical sigmoidal shape predicted by the Avrami equation [Eq. (6)].

Obviously, the values of the adhesive and grain boundary energies are crucial information for understanding agglomeration kinetics. The surface\textsuperscript{14} and grain boundary energies\textsuperscript{22} of both Au and Cu are available in the literature. The interface energy can be calculated from Eq. (1) and contact angle\textsuperscript{13}. Using the surface energy, the contact angle\textsuperscript{13} and Eq. (7), the adhesive energy \( E_{ad} \) between the metal and the SiO\textsubscript{2} can be calculated as follows:

\[
E_{ad} = \gamma_{SO_2} + \gamma_m - \gamma_i = \gamma_m (1 + \cos \theta).
\]

We have tabulated the adhesive energies, the grain boundary energies, the interface energy, and subsequent contact angles in Table I. This information indicates that the grain boundary energy and adhesive energy of the Au films are lower than those of the Cu films. Also, this is supported by the larger dihedral angle \( (\theta_{gb}) \) of the Au film \( (163^\circ) \) in Eq. (8) than that for the Cu film \( (151^\circ) \) at \( 300^\circ \)C

\[
\gamma_{gb} = 2 \gamma_m \cos (\theta_{gb}/2),
\]

where \( \gamma_{gb} \) is the grain boundary energy. Since the Cu film has a higher grain boundary and adhesive energies, it tends to agglomerate through grain boundary grooving by reducing the grain boundary area, compared to the Au film. However, it is still not clear why the Au film agglomerates by void nucleation and fractal growth of void and Cu film agglomerates by grain boundary grooving since the agglomeration is a multifarious process evolving from a nonequilibrium state.

**V. SUMMARY**

The agglomeration behavior of Au and Cu films with a thickness of 5 and 50 nm deposited on a thermal SiO\textsubscript{2} substrate was investigated. It was found that the Au films agglomerate through void nucleation at the initial stage and grow subsequently with snowflake-like branches. After the voids had nucleated at the initial stage, they grew without

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**TABLE I.** Surface, interface, and grain boundary energies of Au and Cu systems.$^a$

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Surface energy of metal ( \gamma_m ) (mJ/m\textsuperscript{2}$^b$)</th>
<th>Contact angle ( \theta ) (°)$^c$</th>
<th>Adhesive energy ( E_{ad} ) (mJ/m\textsuperscript{2}$^d$)</th>
<th>Interface energy ( \gamma_i ) (mJ/m\textsuperscript{2}$^e$)</th>
<th>Grain boundary energy ( \gamma_{gb} ) (mJ/m\textsuperscript{2}$^f$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>300</td>
<td>1537</td>
<td>140</td>
<td>360</td>
<td>1484</td>
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<td></td>
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<td>700</td>
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</tr>
</tbody>
</table>

$^a$The surface energy of SiO\textsubscript{2} is 307 mJ/m\textsuperscript{2} at 1300 °C (see Ref. 23).

$^b$See Ref. 14.

$^c$See Ref. 13.

$^d$See Ref. 22.
further generation of new ones as the annealing time increased. The void branches coalesced with further annealing and finally covered the whole film. An Avrami-type equation was derived to describe the kinetics of agglomeration. The growth morphology of the voids was found to follow a fractal mode with a dimension of 1.7, suggesting that the agglomeration of the Au film corresponds well to a DLA model. By contrast, Cu films are found to agglomerate through the grain boundary grooving mechanism and the final size of the Cu islands depends on the annealing temperature. The different agglomeration behavior for the Au and Cu films is ascribed to the relative differences in the adhesive and the grain boundary energies in the two films.

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