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SUMMARY

Last year we reported the discovery of a new mechanism for obtaining expitaxial films in heteroepitaxial systems with large lattice mismatches. We have called this mechanism epitaxial grain growth (EGG) and have demonstrated that in model experimental systems, metals on mica and alkali halides, EGG can lead to ultrathin continuous films with better crystalline perfection that can be obtained by conventional Volmer-Weber epitaxy (VWE). We were led to our discovery of EGG through our previous AFOSR-sponsored research on surfaceenergy-driven secondary grain growth (SEDSGG) in thin films on amorphous substrates.

Over the past year we have continued our experimental investigations of EGG in model materials systems. We have developed better experimental techniques for quantitive analysis of EGG, especially through the use of quantitative thin film x-ray texture analysis. We have also conclusively demonstrated that the evolution of the orientation of a film undergoing EGG is influenced not only by the film/substrate interface but also by the film/vacuum surface. We have also found that the rate of EGG is higher in thinner films. These results further support the proposed surface-energydriven mechanism.

In the systems investigated so far, we have observed a lower degree of orientation selectivity during EGG than expected from our previous work on SEDSGG on amorphous substrates In order to better understand our results, and in order to determine in which materials systems and under what deposition conditions EGG will be preferred over VWE, we have undertaken the further development of our earlier theoretical models for the evolution of texture in thin films. By numerically calculating the time-dependent evolution of the

distribution of grain orientations and sizes, we are able to simulate SEDSGG in general, and EGG specifically. We can carry out simulations for film/substrate combinations with different materials properties. This is leading to an improved understanding of the conditions which result in reduced defect densities in epitaxial films obtained via EGG.

Over the past year we have obtained a new computer and developed its use in data analysis and for the simulations described above. We have also received funds for an upgrade of our ultrahigh vacuum deposition system which includes cryoshielding, a hot stage, and RHEED. While the upgrade has taken longer than expected, it is now nearly complete and we expect to carry out experiments on EGG in heteroepitaxial films on silicon in the coming year.

I. Epitaxial Grain Growth

Epitaxial grain growth can occur when polycrystalline films are deposited on single crystal substrates and heated so that epitaxially aligned grains grow to consume unaligned grains. Typically, ultrathin but continuous films are deposited at low temperatures and then annealed in situ in the deposition system. Heteroepitaxial systems, with poorly matched lattices, or in which no lattice matching occurs at all, are characterized by island growth, so that films are discontinuous before island coalescence. In these systems, films must sometimes be hundreds of angstroms thick before they are continuous. The EGG process takes advantage of the fact that island spacings are smaller at lower deposition temperatures, so that much thinner continuous films can be obtained. In EGG, epitaxial alignment is accomplished during post-coalescence annealing rather than at a pre-coalescence stage as in Volmer-Weber epitaxy (VWE). In conventional VWE, pre-coalescence alignment requires higher substrate temperatures during deposition. The minimum

continuous film thickness is therefore larger. EGG may thus be the only means of obtaining continuous ultrathin epitaxial films in poorly lattice matched systems.

II. Experiments on Epitaxial Grain Growth

Epitaxial grain growth is an xample of a more general thin film phenomenon known as surface-energy-driven secondary grain growth (SEDSGG), in which surface and interface energy minimization leads to the growth of grains with specific crystallographic orientations. With AFOSR funding, we have extensively studied this phenomenon in polycrystalline films on flat amorphous substrates and on amorphous substrates with artificial surface topography. This work has recently been reviewed in Reference 1. Last year we demonstrated that SEDSGG on single crystal substrates can lead to epitaxial films. We also outlined the extension of the theory of SEDSGG to treat and analyze EGG. A paper describing this work was published this year (2) and is included as a reprint in Appendix I.

Our experimental work to date has been carried out on model materials systems which are relatively easy to work with. We have chosen mica or alkali halides as substrates because they can be cleaved, either inside or outside the deposition system, in order to produce fresh vicinal surfaces. We have chosen metallic films because atomic mobilities in general, and grain boundary mobilities specifically, are high, so that grain growth occurs at relatively low temperatures. The basic phenomena observed in these systems should be the same as in other high mismatch systems.

Based on simple energy arguments (2-3), the rate of growth of an epitaxial grain, dR/dt, is expected to have the following functional dependence on the film thickness h and the temperature T

$$\frac{dR}{dt} = M_0 e^{-Q/\kappa T} \left\{ \frac{\bar{\gamma}_i - \gamma_i}{h} + \frac{\bar{\gamma}_s - \gamma_s}{h} + \gamma_{gb} \left(\frac{1}{\kappa} - \frac{1}{\kappa} \right) \right\}$$

where M_0 is a temperature independent mobility constant, R is the average size of the surrounding grains and

$$\gamma_{\rm gb}$$
 is the average grain boundary energy (energy/area),
 $\gamma_{\rm i}$ and $\bar{\gamma}_{\rm i}$ are the film/substrate interface energy for the
epitaxial grain and the average interface energy for
the surrounding grains, respectively, and,
 $\gamma_{\rm s}$ and $\bar{\gamma}_{\rm s}$ are similarly defined for the film/vacuum surface of
the grains.

This result suggests that

- Grains with orientations which lead to minimum interface energy are favored during epitaxial grain growth.
- ii) The dependence of the film/vacuum surface energy on the crystallographic orientation of the epitaxial grain can also be important.
- iii) The rate of epitaxial grain growth should be higher in thinner films, especially since the normal grain size tends to be fixed and approximately equal to h (3).

Over the past year, we have confirmed these predictions through further experiments on model systems. These experiments were greatly aided by the use of thin film x-ray texture analysis, in addition to transmission electron microscopy and diffraction, in our characterization of our films. By using xray analysis, we have been able to more quantitatively assess the degree to which films had evolved to uniform expitaxial orientations. We have also been able to more readily determine film/substrate orientation relationships. As described in Appendix II, which is a preprint of Reference 4, while we have

found that, in general, the orientation resulting from EGG is that which is found in VWE, this is not always the case. The observed differences are most readily explained in terms of the effects of the film/vacuum interface. The most striking example of this is the observation of epitaxial gold films with (111) surface normals on NaCl substrates with (100) surface normals. While (100) orientations are expected to minimize the film/substrate energy, (111) orientations should minimize the film/vacuum surface energy. Clearly, in the case of the (111)Au||(100)NaCl system, the latter effect dominates.

Also consistent with the predictions listed above is the measured dependence of the degree of EGG-induced alignment as a function of film thickness. In these experiments, we have focused on Cu on mica and used x-ray texture analysis to determine the epitaxial fraction of films of various thicknesses, after isothermal and isochronal in situ anneals. Results for films annealed at 250° C for 3 hours are shown in Figure 1.

One of the surprising results from our experiemnts on model systems is the large number of grains which grow during EGG. SEDSGG on amorphous substrates is highly selective and can lead to very large grains (5), implying very tightly restricted crystallographic orientations. (In SEDSGG on amorphous substrates, the surface normal is restricted, but not the in-plane orientation). The less pronounced selectivity observed so far in our experiments on EGG leads to smaller final grain sizes. While the epitaxial grains have nearly the same orientations, they still meet at low angle grain boundaries, so that reduced selectivity results in a higher density of low angle grain boundaries, which is undesirable. While the films are still better than equally thin films obtained by conventional VWE, their quality could be further improved it selctivity were higher.

In order to better understand our experimental results so far, and to determine what material and deposition characteristics will lead to improved selectivity during EGG, we have further developed the theory of EGG and developed the ability to carry out computer simulations of EGG, as will be described in the next section.

III Modelling of Epitaxial Grain Growth

A more detailed analysis of texture evolution in thin films (6) leads to a result similar to Equation 1, but with the detailed methods of averaging γ_i , γ_s , and R better defined. The time-evolution of the distribution of grain orientations and sizes $[f(\theta, R, t)]$ can be predicted as a function of the dependence of γ_i and γ_s on the crystallographic orientation of a grain (as well as h, γ_{gb} , M_o, Q, and T) by numerically solving the continuity equation for the grain flux in size space (6)

$$\partial f(\theta, R, t) = \partial = 0$$

 $\partial f(\theta, R, t) = 0$
 $\partial t = 0$

We have used this technique to simulate grain growth and to demonstrate the expected evolution of intermediate bimodal distributions and the expected dependence of the average epitaxial grain size on time. A comparison of these quantities at two different film thicknesses is shown in Figures 2 and 3.

We are now using the simulation to determine the type of interface energy/orientation function $[r_i(\theta)]$ that will lead to increased selectivity during SEDSGG and EGG. We will also use this technique to help determine the practical limits on epitaxial alignment via EGG. Figure 4 shows an example of one of our findings. It shows the degree of bimodality (related to the

ultimate epitaxial quality) as a function of the driving force for SEDSGG (proportional to γ_i/h) and as a function of the nature of the interface energy/orientation function, and as a function of inverse film thickness.

In Figure 4, we have used two interface energy/orientation functions. As has been observed experimentally, we have assumed in the simulations that the as-deposited films have uniform crystallographic texture (i.e., all the grains have the same planes parallel to the plane of the substrate), but that the in-plane orientation varies from grain to grain. In this case, the orientation for the grains can be completely described by a single angle for the in-plane rotation θ . The first interface energy/orientation function we used is the Read-Shockley function for which the interface energy varies logarithmically with θ

 $\gamma(\theta) = \gamma_{\min} [1 + K \ln (1 + \theta)] \qquad \theta = 0 \text{ to } 29^\circ$

where γ_{\min} is the minimum interface energy, and therefore the interface energy of the fastest growing secondary grains. The second interface energy function we chose was a step function given by

 $\gamma(\theta) = \{ \begin{array}{c} \gamma_{\text{sec}} & \theta = 0^{\circ} \\ \gamma_{\text{norm}} & \theta = 1 \text{ to } 29^{\circ} \end{array} \right.$

where γ_{sec} and γ_{norm} are the interface energies of the secondary and normal grains, respectively. Comparing experimentally observed bimodality to the results shown in Figure 4 suggests that metals on amorphous substrates have interface energy/orientation functions more similar to the step function than in the case of EGG. Metals on mica and alkali halides have very poor lattice matching and very weak interactions, so that shallow and broad interface energy minima such as in the Read-Shockley formulation, might be expected to

apply. Systems with stronger interactions and better lattice matching, such as fluorides on silicon, might be expected to have deeper and steeper minima, and therefore have greater selectivity during EGG.

Over the next year, we will continue and extend our analyses based on the simulation described above. A manuscript describing our results so far is under preparation and will be supplied when completed.

IV Instrumentation

Over the past year, we have upgraded our computational and experimental facilities for use on this project. We recaived \$60,000 worth of equipment as a donation from Digital Equipment Corporation. This included a DECStation 5000 work station for use in data analysis for simulations as described in the previous section. We have also used an existing rotating anode x-ray generator and pole figure goniometer to develop techniques for quantitative characterization of the epitaxial fraction of our films. Earlier we also received an award from the AT&T Research Foundation to upgrade our ultrahigh vacuum deposition system to include crysoshielding, a hot stage heatable to 900°C and RHEED. This will allow research on EGG in heteroepitaxial films on silicon, as proposed earlier. While this upgrade has taken longer than expected, all of the equipment has been designed and constructed and is now being installed. We expect the upgraded system to be operational in February.

V <u>Future Work</u>

The coming year is the last year of residual AFOSR support for this research. We plan to conclude this project by concluding our experiments on model materials systems and using the computer simulation to analyze our results. Through these analyses we will better define the practical limits on

the quality of films obtainable by EGG, as a function of materials characteristics and processing conditions. We also plan to carry out exploratory experiments on EGG in fluorides deposited on silicon.

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VII <u>Publications This Year</u>

1, 2, and 4 above

VIII Figures

- Fig. 1: Epitaxial fraction transformed as a function of film thickness for Cu films deposited on mica at room temperature and then annealed in situ for 3 hours at 250 C.
- Fig. 2: EGG in a 675 Å film: (a)-(e) evolution of the grain size distribution from monomodal to bimodal and back to monomodal; (f) time dependence of the mean radius of secondary and normal grains. Rescondary is too linear with time and has a maximum time rate of change = 0.49.

- Fig. 3: EGG in a 10 Å film: (a)-(d) evolution of the grain size distribution from monomodal to bimodal and back to monodmodal; (e) time dependence of the mean radius of secondary and normal grains; (f) same as in (e) but showing only the first 700 time steps where secondary grain growth is occuring. R_{secondary} is linear with time in this regime and has a maximum time rate of change = 5.38.
- Fig. 4: Maximum bimodality factor B_{max} (a measure of the ultimate epitaxial quality of a film) from simulations of epitaxial grain growth in films with different driving forces (inversely proportional to film thickness) and two different interface energy vs. orientation functions, as described in the text.



Epitaxial Fraction Transformed vs Film Thickness: Cu on mica; 250°C, 3 hour anneal

Fig 1





