2. Kinetic Phenomena in Thin Film Electronic Materials

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2.1 Surface-Energy-Driven Secondary Grain Growth in Ultrathin (<1000 Å) Films of Silicon and Germanium

Semiconductor Research Corporation (Grant 83-01-033)

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In thin films of semiconductors, normal grain growth is driven by the reduction of the total grain boundary energy and usually leads to grains with sizes roughly equal to the film thickness. We have shown that in sufficiently thin films (< 1000Å) of Silicon and Germanium, a secondary grain growth process leads to the continued growth of some grains to sizes much larger than the film thickness. These secondary grains have near uniform crystallographic texture. We believe that surface-energy anisotropy provides the primary driving force for the growth of these grains, especially in the early stages of growth. That is, grains with orientations that minimize surface energy grow at the expense of other grains. We have shown that the secondary grain growth rate increases sharply with decreasing film thickness and increasing temperature. Unlike metals, addition of impurities (e.g., P in Si) can also lead to an increase in the secondary grain growth rate. We are developing theoretical models for secondary grain growth as a function of the initial microstructure of the film, the composition of the film and film geometry (e.g., film thickness and the width of patterned films). Controlled surface-energy-driven secondary grain growth may provide a low temperature means of producing device quality semiconductor films on insulating substrates.

2.2 Metastable Phase Formation in Lithographically Defined Particles of Semiconductors

National Science Foundation (Grant DMR 81-19285)

Eva Jiran, Carl V. Thompson

When divided into a large number of small particles, materials can undergo phase transformations at substantial departures from equilibrium. It has been shown, for example, that dispersions of small particles of liquid metals can be undercooled to 50 to 80% of their melting temperatures. These undercoolings are achieved due to the isolation of the heterogeneities that catalyze crystal nucleation into a minor fraction of the particles. At high undercoolings, metastable phases can result from configurational freezing (transformation from a liquid to an amorphous solid), through metastable phase nucleation, or due to undercooling-induced rapid solidification. We are using advanced lithography techniques to create samples composed of large numbers of small (including submicron), identical particles of semiconductors for studies of nucleation and metastable phase formation.

2.3 Zone Melting Recrystallization of Silicon and Germanium Films

U.S. Department of Energy (Contract DE-AC02-82-ER-13019)

Harry A. Atwater, Stephen C. Schott, Henry I. Smith, Carl V. Thompson

Techniques for producing device-quality single-crystal films of semiconductors on insulator (SOI) are of interest for multilayer and multimaterial integrated circuits and low-cost, high-efficiency solar cells. Such films can be obtained through directional solidification of confined thin films (zone melting recrystallization, ZMR). While there are analogues to bulk crystal growth in ZMR, there are also phenomena and mechanisms unique to thin-film solidification. We are studying these phenomena in order to develop means of controlling crystal growth in ZMR. Use of lithographically defined patterning, in conjunction with ZMR, permits formation of single crystal silicon films without the use of substrate seeding. We are also investigating the recrystallization of germanium films for use as substrates for epitaxial growth of GaAs.

2.4 Graphoepitaxy of Si, Ge and Model Materials

National Science Foundation (Grant ECS82-05701)

Semiconductor Research Corporation (Grant 83-01-033)

Chee C. Wong, Joyce E. Palmer, Stephen M. Garrison, Harry A. Atwater, Henry I. Smith, Carl V. Thompson

Graphoepitaxy is a process in which an overlayer film is crystallographically oriented by an artificial surface pattern. Graphoepitaxy can involve vapor to solid, liquid to solid, and solid to solid transitions. In experiments on graphoepitaxy we use lithographically defined surface features with periodicities as low as 2000Å. Recent research has focused on the use of artificial surface features in controlling surface-energy-driven secondary grain growth (SEDSGG) in model materials. Periodic patterns with square-wave cross sections increase the driving force for SEDSGG by increasing the surface area. The driving force is increased for grains with specific in-plane orientations as well as texture. Secondary grain growth in thin (~300Å) and smooth Ge films results in grains with predominant (110) and (112) texture. When patterned with square wave surface relief, however, SEDSGG leads to growth of grains with (100) texture which have [100] in plane directions aligned with the grating direction. Greater control of this solid state form of graphoepitaxy may allow the development of low temperature processes for obtaining device quality semiconductor films on insulating substrates.

2.5 Properties of Grain Boundaries with Controlled Orientations and Locations in Thin Silicon Films

International Business Machines, Inc.

James S. Im, Carl V. Thompson, David A. Smith[3]

Ultrathin (< 1000Å) films of silicon are being prepared by zone melting recrystallization (ZMR). Use of film patterning in conjunction with ZMR should allow production of isolated grain boundaries with controlled misorientations and locations. Preparation in thin film form will allow study of grain boundary structure and composition via transmission electron microscopy. Motion of individual boundaries between grains with different textures will also be studied. The misorientation dependence of grain boundary structure, composition and mobility will be studied. These results will be correlated with measurements of electronic properties.

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2.6 Modeling of Grain Formation and Grain Growth in Thin Films

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In thin films, final grain sizes and final grain shapes vary with crystal nucleation and growth rates during film formation. We have modeled two dimensional crystallization and quantitatively shown that grain structures are easily topologically distinguishable when films form under conditions of nucleation site saturation or when constant nucleation rates persist. These results provide a post-formation means of analyzing the conditions under which polycrystalline thin films have been produced. In a second phase of this work, we will model two-dimensional grain growth in generated initial grain structures. Capillarity effects due to surface energy as well as grain boundary energy will be accounted for. Both normal grain growth and secondary grain growth will be modeled.

2.7 Modeling of Beading in Thin Films

Joint Services Electronics Program (Contract DAAG29-83-K-0003)
David J. Srolovitz[5], Carl V. Thompson

Most thin films are thermodynamically unstable in that surface energy minimization favors bead formation. Often, the rate of bead formation can be sufficiently low that beading can be ignored as a restraint on film stability. This may not be true, however, in sufficiently thin films and/or in sufficiently narrow thin film lines. When film dimensions are small, surface to volume ratios are large and the energy change accompanying bead formation increases. The energetics of bead formation from films and lines have been described. It has been shown theoretically and experimentally that the rate of bead formation is strongly influenced by the microstructure of a film.

2.8 Grain Growth in Thin Films and Thin Films Lines

Joint Services Electronics Program (Contract DAAG29-83-K-0003)
Cesar D. Maiorino, Larry Privost, Carl V. Thompson

The thermal and electrical stability of metallic thin films and thin film lines are strongly affected

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by microstructure. Because grain boundary mobilities are high in metals, as compared to semiconductors, secondary grain growth can occur at relatively low homologous temperatures (T/T_m, T_m = the melting temperature), $T/T_m \approx 0.5$, or in relatively thick films ($> 1\mu m$). We have demonstrated that secondary grain growth in 0.75 μm films of Al–2% Cu–0.3% Cr can lead to grains with dimensions greater than 200 μm. Control of surface–energy–driven secondary grain growth in thin film lines with near unity aspect ratios may lead to total elimination of grain boundaries. Such lines would be highly resistant to thermally induced beading and to electromigration. We are investigating the effects of deposition conditions, film composition and annealing conditions on secondary grain growth in Al–2% Cu alloys. These alloys are widely used as interconnect materials in microelectronic devices and circuits.

2.9 Electrical Properties of Interconnect Lines with Controlled Microstructures

Joint Services Electronics Program (Contract DAAG29-83-K-0003)
Cesar D. Maiorino, Larry Privost, Carl V. Thompson

In polycrystalline metallic lines, current assisted diffusion (electromigration) occurs primarily along grain boundaries. Annealing of lines in which the grain size is roughly equal to the line width ($\approx$ 2 μm) can result in the development of a "bamboo" structure in which all grain boundaries are perpendicular to the line axis. Such lines have substantially increased mean times to electromigration induced failure. Unfortunately, the improved reliability of these lines is limited by the persistence of statistically significant numbers of early fails. In this project we are investigating other techniques of microstructural control as means of improving electromigration inhibition. We are also using lines with controlled grain boundary locations to study the effect of grain boundaries on electrical conduction.

2.10 Kinetics of Silicide Formation at Refractory Metal–Silicon Contacts

International Business Machines, Inc.
Lawrence Clevenger, Carl V. Thompson, King-ning Tu[6]

There is considerable current interest in the use of refractory metals or refractory metal silicides as diffusion barriers at metal–silicon contacts in integrated circuits. One method of silicide formation is through reaction of metallic thin films with silicon substrates. This potential application raises fundamental questions about the rate and products of thin film metal–silicon

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reactions. There are four critical parameters in analysis and modeling of these reactions; interdiffusivities, free energy changes, surface energies and interface reaction constants. Of these, the first two parameters are fairly well understood and can be predicted. The purpose of this project is to develop a better understanding and predictive capability for the last two parameters. Surface energies will be determined through silicide precipitation experiments and interface reaction rate constants will be determined through analysis of interface limited reactions of thin films.

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