

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

Final Technical Report

CERAMIC INTERFACES

GRANT NO. DE-FG02-87ER45307

Submitted to:

U.S. Department of Energy
Office of Basic Energy Sciences
Division of Materials Sciences
Washington, D.C. 02545

Submitted by:

Yet-Ming Chiang

Signature _____

Title: Professor of Ceramics
Telephone: (617) 253-6471
Fax: (617) 253-6201
Email: ychiang@mit.edu

Date: _____

TECHNICAL REPORT

During the period of this grant, we significantly advanced the understanding of stable surface amorphous films (SAFs), the existence of which was first postulated and then demonstrated under this program. SAFs are nanometer-thick amorphous films which are characterized by a self-selecting thickness, and a composition and structure distinct from the bulk phases with which they coexist. Importantly, they are present as an equilibrium, disordered phase below bulk solidus temperatures where all other phases in the system are crystalline. They are true surface phases which coexist in thermodynamic equilibrium with the bulk phases. We have shown that SAFs form in a number of binary oxide systems, and that they play an important role in the processing of materials (e.g., solid-state activated sintering in ZnO-Bi₂O₃) and in forming surface-active layers in supported catalyst systems. These experimental results as well as a theoretical model for the stability of SAFs have now been published (see list of papers). We believe that SAFs can be controlled and manipulated in a wide range of systems, with potential applications in nanotechnology, MEMS, microelectronics, adhesion, and colloidal crystals. The most significant research results under this grant are as follows:

Selection Criteria for Systems Exhibiting Equilibrium Surface Amorphous Films We have systematically evaluated major interactions that determine the stability of surface films, including dispersion (vdW) forces, short-range interactions, and volumetric amorphization energies. Based on the signs and magnitudes of these interactions, we proposed the following criteria for film stability: The existence of an “equilibrium” thickness firstly suggests that the film formation lowers the surface energy, and secondly requires an attractive long-range interaction. The presence of a positive dispersion force acting to thin the film is critical close to and above the solidus temperature, but relatively unimportant well below the solidus where the amorphization energy is a dominant consideration preventing unconstrained film thickening. In this temperature regime, additives with low fusion entropies are essential to SAF stabilization.

To test these criteria, we have pursued experiments in six oxide systems: ZnO-Bi₂O₃, Fe₂O₃-Bi₂O₃, TiO₂-WO₃, Al₂O₃-MoO₃, SiO₂-TiO₂, and Bi₂O₃-SiO₃. The systems and experimental conditions were chosen so that relative surface energies, the signs and magnitudes of vdW forces, fusion entropies of film-forming additives, temperature, and saturation were systematically varied. The observed film stability is consistent with the proposed model. Additionally, the measured thickness of subsolidus films has been observed to decrease with increasing free energy of fusion for the film-forming additive in the order $h(\text{SiO}_2 \text{ on Bi}_2\text{O}_3) > h(\text{Bi}_2\text{O}_3 \text{ on ZnO, Fe}_2\text{O}_3) > h(\text{WO}_3 \text{ on TiO}_2) > h(\text{MoO}_3 \text{ on Al}_2\text{O}_3)$. This quantitative correlation further supports our model.

Bi₂O₃-Enriched Films on ZnO Single Crystals Initially we studied films formed on surfaces of fine powders. Subsequently, we focused on single crystal experiments. These experiments have revealed the following results. Auger surface analysis showed that the composition of the Bi-enriched surface film on ZnO (11 $\bar{2}$ 0) surfaces is distinctly Zn-rich (~18 mole % Bi₂O₃) compared to the near-eutectic equilibrium bulk liquid (~83 mole % Bi₂O₃). A combination of Atomic Force Microscopy (AFM) and optical microscopy with polarized light showed that the bulk (eutectic) liquid does not completely wet the ZnO (11 $\bar{2}$ 0) surface, providing additional evidence for the co-existence of bulk nonwetting liquid with a SAF of “equilibrium” thickness.

Third, we observed the epitaxial growth of $\delta\text{-Bi}_2\text{O}_3$ micro-crystals on the ZnO ($11\bar{2}0$) surface, supporting the previous assumption that epitaxy stabilizes the bismuth-enriched films on this surface (lowering the corresponding film/crystal interface). This result explains the previously observed anisotropy, wherein the ZnO ($11\bar{2}0$) surfaces are preferred for SAF formation.

Interpretation of SAFs as True Surface Phases Combining the above single crystal experiments and our previous results from powder experiments, we can now conclude that surface films should not be viewed simply as a confined bulk liquid slightly modified in composition and structure by the adjacent crystal. SAFs are true surface phases co-existing with one or more bulk phases. In the two-component systems studied, the SAFs have been observed to co-exist with one or two bulk phases. Thermodynamic analysis shows that a third (surface) phase is thermodynamically allowed in two-component equilibrium due to the additional degree of freedom provided by having a surface. Correspondingly the film thickness (or nonhydrostatic pressure) becomes an additional intensive variable, and the composition and structure of the “liquid-like” surface films are distinct from that of the bulk liquid phase. This work provides a new theoretical perspective to understand surface and intergranular amorphous films.

Temperature Dependence of Film Thickness: One of the important testable criteria for theoretical models of SAF stability is the temperature dependence of the film thickness. Below the solidus temperature, the amorphous film has an excess volumetric free energy relative to the crystalline bulk phases, the magnitude of which increases with undercooling. Thus the SAF is expected to thin as temperature decreases. A systematic investigation of the temperature dependence of film thickness was performed for Bi_2O_3 on ZnO . In order to identify any kinetic limitations to equilibration, the SAF was allowed to approach its equilibrium state from both lower and higher temperatures. In the first instance, samples were directly heated to the annealing temperature and equilibrated for long times. In the second, samples were firstly fired at a higher temperature of 780°C , at which thicker films are known to form, and then the temperature was lowered to the equilibration temperature. Consequently, the measured mean thicknesses for the two types of samples should bound the true equilibrium values. Additionally, statistical evaluations were performed to give the confidence intervals of each measured datum.

The results are shown in Figure 1. Note firstly that there is a clear temperature dependence to the SAF thickness, decreasing with decreasing temperature. This is qualitatively consistent with our model (ref. 1 in the list of publications) in which the volumetric free energy of amorphization plays a key role in determining SAF thickness. Note that as the temperature is reduced, the range of thickness measured by the two types of experiments broadens, indicating that equilibration kinetics may still be limiting at the lower temperatures. These experiments were conducted in the presence of crystalline bismuth oxide secondary phase, which acts as a sink for the excess film-forming constituents. Transport to the sink may be the kinetically limiting step during equilibration.

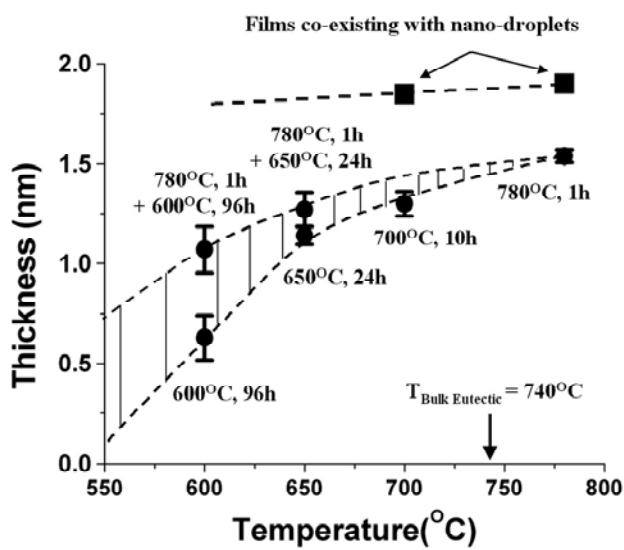


Figure 1. (left) ● Equilibrium thickness vs. temperature. Bars represent 75% confidence intervals; ■ Thickness of the films co-existing with nano-droplets.

Figure 2. (above) A non-wetting nano-droplet coexisting with a surface film.

Surface Phase Separation As a Critical Test of the Model: We also observed a second class of films forming in equilibrium with nano-scale droplets of bismuth-rich oxide, Figure 2. These films are distinguished by having a significantly greater thickness, and less temperature dependence of thickness, compared to the films equilibrated with crystalline phase (Figure 1). They serve as a second confirmation of the proposed model for the following reasons. When there is an excess of Bi_2O_3 in the surface film, but it is not allowed to crystallize upon cooling, the volumetric free energy contribution which causes film thinning cannot be as great. While other interactions across the SAF will still act to reduce thickness, the temperature dependence is not as great as when a bulk, crystalline, sink for the excess glass is present. This new observation may be considered a case of *phase separation* within the SAF.

Overall, these new results can be analysed within the context of a more detailed theoretical model for SAF stability, with phenomenological similarities to multilayer adsorption, prewetting and surface melting. The next goal in this research is formulate a model that allows the prediction of these surface phenomena from bulk phase thermodynamics.

Papers Published and Submitted Under This Grant (June 1999 – June 2002)

1. Jian Luo, and Yet-Ming Chiang, "Equilibrium-thickness Amorphous Films on $\{1\ 1\ \bar{2}\ 0\}$ Surfaces of Bi_2O_3 -Doped ZnO ," *Journal of European Ceramic Society*, **19**, 997-701 (1999).
2. Jian Luo, Haifeng Wang, and Yet-Ming Chiang, "Origin of Solid State Activated Sintering in Bi_2O_3 -Doped ZnO ," *Journal of American Ceramic Society*, **83** [4], 916-20 (1999).
3. Jian Luo, and Yet-Ming Chiang, "Stability of Equilibrium-Thickness Surface and Intergranular Amorphous Films in Ceramics and Their Role in Activated Sintering," *Sintering Technologies 2000, The 1999 Conference Proceedings*, in press (2000).

4. H. D. Ackler and Y.-M. Chiang, "Effect of Initial Microstructure on Final Intergranular Phase Distribution in Liquid Phase Sintered Ceramics," *J. Am. Ceram. Soc.*, **82**[1] 183-189 (1999).
5. J. Luo and Y.-M. Chiang, "Existence and Stability of Nanometer-Thick Amorphous Films on Oxide Surfaces," *Acta Mat.*, **48**, 4501-4515 (2000).
6. J. Luo and Y.-M. Chiang, "Stabilization of Surface Films in Ceramics," pp. 419-426 in *Ceram. Transactions*, Vol. 118, Grain Boundary Engineering in Ceramics, American Ceramic Society, 2000.
7. J. Luo, H. Wang, and Y.-M. Chiang, "Stability of Equilibrium-Thickness Surface and Intergranular Amorphous Films in Ceramics and Their Role in Activated Sintering," Sintering Technologies 2000, Proceedings of Sintering '99 Conference, Nov. 1-3, 1999, Pennsylvania State University, State College, PA.

Other Highlights related to this Program:

Jian Luo, a graduate student supported by this program, received First Prize, Graduate Student Poster Contest, Gordon Research Conference on Solid State Studies in Ceramics, Kimball-Union Academy, Meriden, NH, August 1999.

The 2001 Ross Coffin Purdy Award of the American Ceramic Society, for best scientific paper, was awarded in April 2001 to H. D. Ackler and Y.-M. Chiang, for the paper "Effect of Initial Microstructure on Final Intergranular Phase Distribution in Liquid Phase Sintered Ceramics," *J. Am. Ceram. Soc.*, **82**[1] 183-189 (1999). This work was supported by the subject BES program.

Jian Luo received a Ph.D. degree from MIT for his thesis: *Existence and Stability of Nanometer-Thick Disordered Films on Oxide Surfaces* in June 2001. He is currently a faculty member in the Materials Science and Engineering Department at Clemson University.