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Experimental and Theoretical Studies of Nucleation in Supercooled Liquid Silicon

Final Program Report

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DISCLAIMER

SUMMARY

The original objectives of the present program consisted of two specific nucleation-related research activities; (1) to provide a set of experimental data that will enable the quantitative examination of classical nucleation theory, and (2) to describe the phenomenon of nucleation by developing general expressions of nucleation that include both the thermal and athermal components and that correctly consider and incorporate the transient effects that arise from the nonstationary cluster distribution profile.

As presented below with more details, we were able to accomplish these experimental and analytical tasks; however, we have thus far published only a fraction of our work and are presently in the process of preparing several manuscripts that deal with the remaining material. (This situation stems primarily from the fact that the PI has been quite intensely involved in educating and assisting a large number of companies and research institutions during the past five years on mastering and implementing a particular laser crystallization method, which has been invented and developed in the PI's laboratory.)

In addition to the above activities outlined in the original proposal, we were able to also identify and pursue two new opportunities regarding nucleation in condensed systems during the course of the program. The first contribution dealt with the formulation of numerical modeling of nucleation that captures the stochastic and kinetic aspects of the phenomenon. This work has lead to an invited presentation during the fall MRS Meeting in December 1999 and a publication in Applied Physics Letters.

The second body of additional work involved excimer-laser induced melting and solidification of thin metallic films. Our findings to date reveal that we can systematically induce and analyze true nucleation of solids in laser quenched metallic films (that are primarily but not exclusively on SiO_2). We believe that these results speak volumes about the opportunities we have at hand with the pulsed-laser/thin film experimental approach for making further contributions to the field of nucleation in condensed systems. We are presently in the process of preparing several manuscripts that report these findings.

DESCRIPTION OF RESEARCH ACCOMPLISHMENTS

1. Experimental Characterization of Nucleation Rates in Supercooled Liquid Si:

Utilizing the improved experimental procedures and equipment outlined in the proposal, we have conducted and analyzed isothermal and nonisothermal nucleation experiments over a nucleation frequency range of approximately five orders of magnitude. The results indicate that the heterogeneous nucleation mechanism dominates over the range of conditions under which

the phenomenon is investigated, and that the heterogeneous extension of CNT appears to adequately describe the findings with a contact angle between 62 and 70 degrees. The results are meaningful in that they constitute the most systematic and quantitative characterization and analysis of nucleation in condensed systems to date. (Our findings indicate that the argument for homogeneous nucleation made in a widely referred earlier work by Stiffler et. al. (PRL 60, 2519 (1988)) regarding the nature of nucleation in pulsed laser quenched Si films is likely be incorrect.) We are in the process of preparing a manuscript that communicates the findings we have made in this portion of the work. The bulk of the experimental work is contained and articulated in John Leonard's thesis (attached in this report), and we are presently in the process of preparing manuscripts on the findings.

2. Analysis of Athermal and Transient Nucleation in Condensed Systems:

The most significant outcome of our effort in this component of the program involved development of a simple graphical method for capturing and conveying the thermal/athermal mechanisms and transient/stationary modes of nucleation. This graphical approach involves construction of a mechanism-mode diagram (the process of which requires no more information than that needed for calculating the steady-state nucleation rates and isothermal induction times) onto which the quench-rate vs. temperature trajectory of any thermal history can be projected for analysis. At the simplest level, the diagram can be utilized in order to identify the conditions under which the use of steady-state nucleation rates and the omission of consideration of athermal nucleation mechanism are justified. This capability was demonstrated by constructing such mechanism-mode diagrams for Si, lithium disilicate and $Au_{81}Si_{19}$ systems, and comparing the resulting information to those that are obtained via exact numerical simulation.

We were able to also demonstrate that it is possible to estimate the population of quenched-in crystal clusters that originate during the formation of the glass based on the use of mechanism—mode diagrams. Such information is of relevance as it is recognized that the mode and rates of crystallization of a glass can depend on the presence and population of such clusters. Previously, obtaining such information required extensive simulations of cluster dynamics for each specific quenching condition or involved analytical treatments that are approximate and limited in applicability. In contrast to these approaches, the mechanism-mode diagram-based analysis provides the relevant information in a manner that is both simple and intuitive for arbitrary quenching conditions. Some of the findings were presented at the 1998 and 1999 Fall MRS meetings. Much of the analysis is presented in the appendix section of M. A. Crowder's thesis (attached in this report) and we are presently in the process of preparing manuscripts on the topic.

3. Stochastic Modeling of Solid Nucleation in Supercooled Liquids:

We have also succeeded in formulating and developing a three-dimensional numerical model that incorporates algorithms to simulate nucleation and growth in supercooled liquid in a manner that properly accounts for the stochastic nature of nucleation. In contrast to previously formulated numerical models, no empirical or deterministic conditions for nucleation are imposed; nucleation events occur solely based on preassigned nucleation kinetics. Such a feat is accomplished by first calculating the probability of nucleation in each and every liquid node during each time step using the Poisson expression, and then triggering nucleation if and only when the random number assigned to a node for the time step is less than the calculated nucleation probability.

The basis of the model is quite general, and as such, it should be possible to extend the model to other first-order phase transitions, and also incorporate additional or alternate nucleation scenarios and mechanisms (such as competitive nucleation between various phases and/or heterogeneous mechanisms, transient and/or athermal nucleation, and nucleant-initiated growth from randomly distributed inoculants). The model simply requires the capability to quantitatively evaluate a probability of success within the matrix of the metastable parent phase for a given spatial domain and time interval.

An invited talk (title: Modeling Solid Nucleation and Growth in Supercooled Liquid) was presented on the model at the 1999 Fall MRS conference (Symposium on "Nucleation and Growth Processes in Materials") held in Boston. Also, a contributed talk (title: 3D Numerical Modeling of Laser Crystallization Processes in Si Thin Films) was presented on the model at the 2000 Spring MRS conference (Symposium on "Flat Panel Display Materials") held in Boston. Two papers have been published on the model.

4. Pulsed-laser Induced Melting and Solidification of Thin Metallic Films:

Encouraged in part by the ease with which we were able to systematically induce and analyze nucleation of solids in supercooled liquid Si, we have conducted a set of simple excimer laser irradiation experiments involving a select number of metallic films (Primarily Al and Cu) on SiO_2. The resulting experimental findings reveal definitively that it is indeed possible to also induce and analyze nucleation-initiated solidification of these metallic films, provided that the incident energy density of the beam is sufficiently high to induce complete melting of the films. We firmly believe that these results (shown below in Fig. 1) point to the unprecedented opportunity one has at hand for further scrutinizing the nature and details of nucleation in condensed systems as well as to study rapid solidification of materials in general. We have presented some of the findings at 2001 and 2003 Spring MRS meetings and are presently in the process of preparation several manuscripts on the topic.

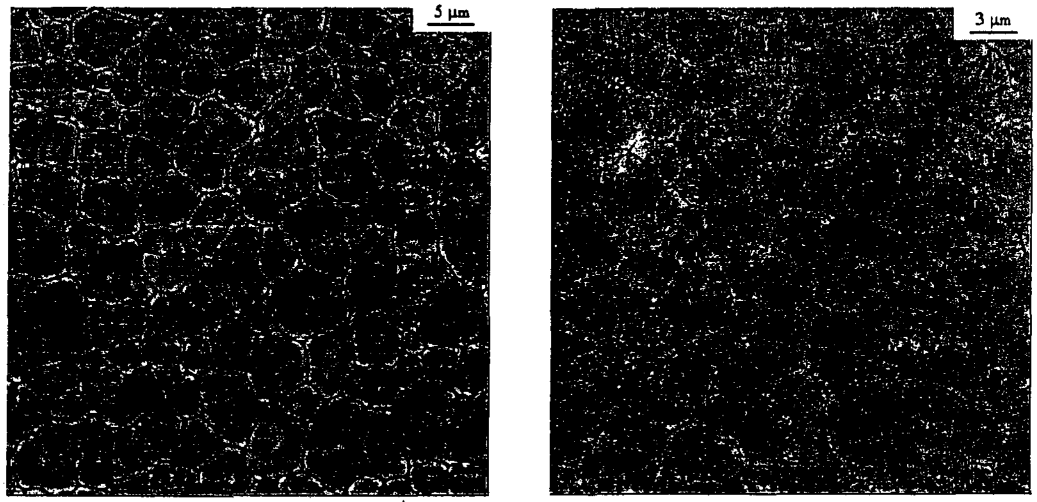

Figure 1. AFM micrographs that reveal the polycrystalline microstructure formed via spontaneous nucleation and growth of solids in supercooled liquid matrix: (left) 200 nm Al on SiO_2, and (right) 100 nm Cu on Ta coated (7 nm) SiO_2.

PERSONS WHO WERE SUPPORTED PRIMARILY THROUGH THE PROGRAM

Dr. John P. Leonard, Ph.D., 2000 (assistant professor, University of Pittsburgh).

Dr. Mark A. Crowder, Ph.D., 2001 (researcher, Sharp Laboratories of America).

PUBLICATIONS RESULTING FROM THE PROGRAM (SINCE 1998)

"Stochastic modeling of solid nucleation in supercooled liquids," J. P. Leonard and James S. Im, *Applied Physics Letters*, **78**, 3454, (2001).

"Modeling solid nucleation and growth in supercooled liquids," J. P. Leonard and James S. Im, Mater. Res. Soc. Symp. Proc., **580**, (1999).

"On determining the relevance of athermal nucleation in rapidly quenched liquids," James S. Im, Vikas Gupta, and M. A. Crowder, *Applied Physics Letters*, **72**, 662, (1998).

"Thermal and Athermal Nucleation in Condensed Systems," James S. Im, Vikas Gupta, and M. A. Crowder, to be submitted.

"Estimating the distribution of quenched-in critical clusters using mechanism-mode diagrams," M. A. Crowder and James S. Im, to be submitted.

"Construction and utilization of a nucleation mechanism-mode diagram," M. A. Crowder and James S. Im, to be submitted.

"Kinetic analysis of glass formation using mechanism-mode diagrams," M. A. Crowder and James S. Im, to be submitted.

"The nature and rates of solid nucleation in laser-quenched Si films on SiO_2," J. P. Leonard and James S. Im, to be submitted.

"Excimer-laser induced melting and solidification of thin aluminum films on SiO_2" J. B. Choi and James S. Im, to be submitted.

"On the effect of nuclei orientation in heterogeneous nucleation of solids in supercooled liquids," J. B. Choi and James S. Im, to be submitted.

"The microstructure of nucleated grains in laser-quenched Si films," Sharona Hazair and James S. Im, to be submitted.

INVITED PRESENTATIONS RESULTING FROM THE PROGRAM (SINCE 1998)

Modeling solid nucleation and growth in supercooled liquids," J. P. Leonard and James S. Im, 1999 Fall MRS Conference (Symposium on "Nucleation and Growth Processes in Materials")

"On the analysis and manipulation of crystallographic orientation in SLS-processed Si, CU, and Al films," James S. Im, B. A. Turk, J. B. Choi, P. C. Van der Wilt, J. Nakayama, M. A. Crowder, R. S. Sposili, and A. B. Limanov, 2002 Spring MRS Conference (Symposium on "Texture and Microstructure in Electronic and Magnetic Films").

CONTRIBUTED PRESENTATIONS RESULTING FROM THE PROGRAM (SINCE 1998)

"Kinetic Analysis of Glass Formation Using Nucleation Mechanism-Mode Diagrams," M. A. Crowder and James S. Im, 1998 Fall MRS Conference (Symposium on "Bulk Metallic Glasses").

"Crystallization of Glasses: Estimating the distribution of quenched-in critical clusters using mechanism-mode nucleation diagrams," M. A. Crowder and James S. Im, 1999 Fall MRS Conference (Symposium on "Nucleation and Growth Processes in Materials").

"Crystallization Analysis of Amorphous Si Films Obtained Through Ion Irradiation and Excimer Laser Irradiation: Implications for Amorphization Mechanisms," J. P. Leonard, John C. Leu and James S. Im, 1999 Fall MRS Conference (Symposium on "Nucleation and Growth Processes in Materials").

"3D Numerical Modeling of Laser Crystallization Processes in Silicon Thin Films," J. P. Leonard, A. B. Limanov and James S. Im, 2000 Spring MRS Conference (Symposium on "Nucleation and Growth Processes in Materials").

"Microstructural Manipulation of Copper Films via Pulsed-Laser induced Melting and Solidification," J. W. Lau, M. A. Crowder, A. B. Limanov, and James S. Im, 2001 Spring MRS Conference (Symposium on "Materials, Technology, and Reliability for Advanced Interconnects and Low-K Dielectrics").

"Interfacial Microcrystallization Encountered During Excimer-Laser Induced Rapid Solidification of Thin Si Films," Hans S. Cho, Dongbyum Kim, A. B. Limanov, M. A. Crowder and James S. Im, 2001 Spring MRS Conference (Symposium on "Advanced Materials and Devices for Large-Area Electronics").

"Grain Boundary and Texture Optimization of Al films via Excimer Laser Irradiation," J. B. Choi and James S. Im, 2003 Spring MRS Conference (Symposium on "Materials, Technology, and Reliability for Advanced Interconnects and Low-K Dielectrics").