DEVELOPMENT AND USE OF IMAGE SCANNING ELLIPSOMETER
TO STUDY THE DYNAMICS OF HEATED THIN LIQUID FILMS

Final Report

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ABSTRACT

The general objective of this research was to study the characteristics of evaporative phase change in ultra-thin films. The immediate objective was to develop and use microscopic image processing systems (IPS) to measure film thickness profiles. The IPS has two possible configurations: an image analyzing interferometer (IAI) and/or an image scanning ellipsometer (ISE). Both pure liquid films and the formation of sol-gel (xerogels) coatings were studied.

An IAI was developed and used to measure the thickness profiles of equilibrium and evaporating liquid films under various conditions. The design and construction of an ISE was also completed and the system was successfully tested by measuring the thickness profile and the refractive index of a non uniform solid film. The profiles of both wetting and partially wetting draining isothermal films were also measured using the ISE. The profiles of the wetting films were analyzed to obtain the dynamics of transport processes in completely wetting thin films. The analysis of the nonwetting profiles continues. TEOS based sol-gels were fabricated in bulk as well as deposited as films on silicon wafers by spin-coating. We found that the properties of the final xerogel films are very sensitive to the processing conditions.

REVIEW OF PROGRESS

The long-term objectives of the research were to determine the heat transfer characteristics and stability of evaporating ultra-thin films. Some of these films may form permanent coatings like xerogels which would be of use as interlayers in the semiconductor industry and as porous flow control elements in passive heat exchangers like heat pipes. The immediate objective was to develop and use a microscopic image-processing system (IPS) to measure the film thickness profile. These measurements are important because the thickness profile gives information on the stability of the thin films and the transport processes in the liquid film. For solid coatings, the transport processes, that control the formation and final properties of the coatings, are strongly effected by intermolecular and interfacial forces.

The results of the research have been published in a broad range of publications because they cover not only the development of a unique experimental technique but also concern a fundamental study in interfacial transport phenomena. For example, we found that the critical boundary condition in the contact line region was not sufficiently well defined. However, since it was needed to understand fluid flow and change-of-phase heat transfer in our research on thin films, we rectified this deficiency. These results were discussed in the publications coded P5, P6, and P8, and P9, which are listed below.

The IPS has two parts: an image analyzing interferometer (IAI) and an image scanning ellipsometer (ISE). The design and use of the IAI was discussed in numerous publications sent to DOE, which are listed below as P1, P2, P3, P4, P7 and P11. We found that the convenience and efficiency of microcomputer enhanced video microscopy naturally led to a better understanding of the transport processes in the contact line region. We also found that the processes of change-of-phase heat transfer and fluid flow in thin films are intrinsically connected because of their common dependence on the intermolecular force field.

The ISE is a rapid full-field imaging technique, which we developed with high spatial resolution, that enables measurements of the changes in the very thin liquid film thickness profiles associated with instabilities, fluid flow, evaporation and drying. The initial ISE (originally called IAE in our initial report DOE/ER/14045-1), which was designed for proof of principle testing, was configured using an available null ellipsometer modified with laboratory optical equipment. We added an autocollimator to obtain accurate alignment, a video camera, and a long working distance microscope to improve resolution and magnification. After many modifications, the first generation ISE system was described in P10 and P15. The use of this ISE technique to measure the thickness profile and refractive index of a non uniform thin solid film was discussed in P10 and DOE/ER/14045-5. The ISE results were evaluated by comparing the experimental results with those obtained using our interferometer and also with those supplied by the manufacturer. The profiles of both wetting and partially wetting draining isothermal films were also measured. The profiles for the wetting films were analyzed and the results were published. This work was detailed in P14 and P16. Three additional papers concerning the ISE are P12, P13 and P17. The doctoral student, who developed the ISE, completed his thesis (P15). The analysis of the nonwetting profiles (P16), which we find challenging,

continues. An invited chapter in an upcoming book on microscale heat transfer (P18) integrates the above material (P1- P17) into the field of the effect of interfacial phenomena on change of phase heat transfer.

Since the ISE can measure thinner films than the IAI, we decided to emphasize the further development, evaluation and use of the ISE technique. Considerable development effort resulted in the construction and use of a very flexible new ISE instrument to study the formation of thin coatings. One of the most exciting current research topics is the development of spin-on silica xerogel films for use as interlayer dielectrics in the semiconductor industry and as porous flow control elements in heat exchangers. Therefore, we have been developing techniques to fabricate and characterize spin-on xerogel films which we plan to study using the ISE. Our initial results were reported in P19 (PR 19, DOE/ER/14045-13) and P20 listed below and sent to DOE. Finally, the above results have been used to write a new proposal that has been submitted to DOE and is currently under review.

The two doctoral students who were responsible for the development of the IPS completed their theses. A third doctoral student, who was responsible for the sol-gel research, will present his thesis in August, 1998.

LIST OF PUBLICATIONS/PRESENTATIONS/DOE REPORTS

PUBLICATIONS

- P1) "Microcomputer Enhanced Optical Investigation of Transport Processes in Thin Liquid Films", M. Sujanani and P.C. Wayner, Jr., pp. 79-86, DOE CONF-9005183, Proceedings of Eighth Symposium on Energy Engineering Sciences, Argonne National Laboratory, Argonne, IL, May 9-11, 1990.
- P2) "Interfacial Phenomena in an Evaporating Thin Film", M. Sujanani, *Ph.D. Thesis*, Rensselaer Polytechnic Institute, Troy, NY, 1990. Abstract in Appendix A of DOE/ER/14045-2.
- P3) "Microcomputer Enhanced Optical Investigation of Transport Processes with Phase Change in Near-Equilibrium Thin Liquid Films", M. Sujanani and P.C. Wayner, Jr., *J. Colloid and Interface Science*, **143**, 472-487, 1991. (DOE/ER/1045-3)
- P4a) "Transport Processes and Interfacial Phenomena in an Evaporating Meniscus", M. Sujanani and P.C. Wayner, Jr., paper preprint AIAA 91-4002 presented at 1991 ASME/AIChE/AIAA *National Heat Transfer Conference*, Minneapolis, MN. (Sent to DOE as a manuscript)
- b) "Transport Processes and Interfacial Phenomena in an Evaporating Meniscus", M. Sujanani and P. C. Wayner, Jr., rewritten version of P4a, *Chemical Engineering Communications*, **118**, 89-110, 1992. (Sent to DOE as a reprint).

- P5a) "Evaporation and Stress in a Small Constrained System", P.C. Wayner, Jr., Extended Abstract, pp. 269-272, in Paper Summaries, *IS&T's 44th Annual Conference*, May 12-17, 1991, St. Paul, MN. (Sent to DOE as DOE/ER/14045-4) .
- b) P5a published as part of a book of selected articles *IS&T's Proceedings of the 44th Annual Conference, Symposium on Coating Technologies for Imaging Materials*, Edited by J. Truong, IS&T, Springfield, VA, 22151, 1991, pp. 174-181.
- P6) "Spreading of a Liquid Film on a Substrate by the Evaporation-Adsorption Process", P.C. Wayner, Jr. and J. Schonberg, *J. Colloid and Interface Science*, **152**, 507-520, 1992. (Sent to DOE as a manuscript and reprint).
- P7) "Interfacial Phenomena, Evaporation and Stress in a Constrained System", S. DasGupta, I.Y. Kim, and P.C. Wayner, Jr., preprint #AIAA 92-4053, Washington, 1992. (Sent to DOE as a preprint)
- P8) "Evaporation and Stress in the Contact Line Region", P. C. Wayner, Jr., in "Pool and External Flow Boiling" V. K. Dhir and A.E. Bergles Editors, Engineering Foundation by ASME, New York, New York, 1992, pp. 251-256. DOE/ER/14045-6
- P9) "Spreading of a Liquid Film with a Finite Contact Angle by the Evaporation/Condensation Process", P.C. Wayner, Jr., *Langmuir*, **9**, 294-299, 1993. (Sent to DOE as a manuscript and reprint).
- P10) "Image Scanning Ellipsometry for Measuring Non-Uniform Film Thickness Profiles", A.H. Liu, P.C. Wayner, Jr., and J.L. Plawsky, *Applied Optics*, **33**, 1223-1229, 1994. (Sent to DOE as a manuscript and reprint).
- P11) "Use of the Augmented Young-Laplace Equation to Model Equilibrium and Evaporating Extended Menisci", S. DasGupta, J.A. Schonberg, I.Y. Kim, And P.C. Wayner, Jr., *J. Colloids and Interface Science*, **157**, 332-342, 1993. (Sent to DOE as a reprint)
- P12) "Microscopic Image Processing System for Measuring Nonuniform Film Thickness Profiles: Image Scanning, Ellipsometry", Liu, A.H., J. Plawsky, and P.C. Wayner, Jr., Proceedings of 11th Symposium on Energy Engineering Science, Conf.-9305134, pp. 107-204, Department of Energy, Argonne National Laboratories, Argonne, IL, May 1993.
- P13) "Microscopic Image Processing Systems for Measuring Nonuniform Film Thickness Profiles", A.H. Liu, J.L. Plawsky, and P.C. Wayner, Jr., Proceedings of the 10th International Heat Transfer Conference, Brighton, England, **2**, 262-272, 1994, Edited by G. F. Hewitt, Institution of Chemical Engineers, Rugby, Warwickshire, UK. (Sent to DOE as a conference paper, DOE/ER/ 14045-8)
- P14) "Image Scanning Ellipsometer for Measuring Transient Non-uniform Very Thin Liquid Film Thickness Profiles", A.H. Liu, P.C. Wayner, Jr., and J.L. Plawsky, *Physics of Fluids A*, **6**, 1963-1971, 1994. (Sent to DOE as a manuscript and reprint)

- P15) "Design, Development, and Applications of Image Scanning Ellipsometer for the Measurement of Thin Film Thickness Profiles", A. H. Liu, *Ph.D. Thesis*, Rensselaer Polytechnic Institute, Troy, NY, 1994. Abstract in Appendix A of DOE/ER/14045-10.
- P16) "Drainage of a Partially Wetting Film: Dodecane on Silicon", A.H. Liu, P.C. Wayner, Jr., and J.L. Plawsky, *I&EC Chemistry Research*, Vol. 35, #9, pp. 2955-2963, 1996. (Sent to DOE as a manuscript and reprint)
- P17) "Image Processing Techniques for Measuring Non-Uniform Film Thickness Profiles", Nitta, S.V., Liu, A.H., Plawsky, J., and Wayner, P.C., Jr., *Proceedings of 14th Symposium on Energy Engineering Sciences: Mechanical Sciences, Solids and Fluids*, DOE CONF-9605186, pp. 199-206, 1996.
- P18) "Interfacial Forces and Phase Change in Thin Liquid Films," P. C. Wayner, Jr., Invited submission as Chapter 6 in "Microscale Energy Transport" by C. L. Tien, F. W. Gerner and A. Majumdar, Taylor & Francis, Washington, DC, 1998. (Sent to DOE as a manuscript)
- P19) "Fabrication and Characterization of Spin-on Silica Xerogel Films", S. Nitta, W. N. Gill, P.C. Wayner, Jr. and J.L. Plawsky, Presented at the 1998 Spring MRS Annual Meeting, San Francisco, CA, April 14-21, To be published in the Proceedings (Sent to DOE as a manuscript, DOE/ER/14045-13)
- P20) "Surface Modified Spin-on Xerogel Films as Interlayer Dielectrics", Jain, A., Pisupatti, V., S. Nitta, W. N. Gill, P.C. Wayner, Jr. and J.L. Plawsky (sent to DOE as a manuscript)

PRESENTATIONS

- PR1) "Fluid Flow in Ultra Thin Films", M. Sujunani and P.C. Wayner, Jr., Presentation 167C-b, 1989 Annual Meeting of A.I.Ch.E., Nov. 5-10, San Francisco, CA.
- PR2) P1 above
- PR3) P4a above
- PR4) P5a above
- PR5) P7 above was presented at the ASME/AIChE National Heat Transfer Conference, August 9-12, San Diego, CA, 1992.
- PR6) P8 above was presented at the Engineering Foundation Conference on Pool and External Flow Boiling, Santa Barbara, CA, March 22-27, 1992.
- PR7) P9 above was presented at the Research Conference on Capillarity and Wetting, Dynamical Phenomena, Arnhem, Netherlands, September 1 -6,1992 at no expense to DOE.

PR8) P9 above was presented at the AIChE 1992 Annual Meeting, November 1-6, Miami Beach, FL.

PR9) P12 above

PR10) "Image Scanning Ellipsometer for the Measurement of Thin-Film Thickness Profiles", A.H. Liu, P.C. Wayner, Jr., and J.L. Plawsky, Optical Society of America Annual Meeting, Toronto, Canada, Aug. 1993 (P10 above).

PR11) "Image Scanning Ellipsometer for the Measurement of Thin-Film Thickness Profiles", A.H. Liu, P.C. Wayner, Jr., and J.L. Plawsky, 1993 Annual Meeting of AIChE, St. Louis, MO, Nov. 1993 (P14 above).

PR12) "Development and Use of Image Scanning Ellipsometer to Study the Dynamics of Heated Thin Liquid Films", OPA Peer Review Assessment, Gaithersburg, MD, Nov. 16-18, 1993.

PR13) P 13 above.

PR14) "Film Thickness Profiles for a Partially Wetting System, Dodecane on Silicon: An Application of Image Scanning Ellipsometer", A.H. Liu, P.C. Wayner, Jr., and J.L. Plawsky, AIChE 1994 Annual Meeting, November 13-14, San Francisco, CA.

PR15) "Simulating Drainage of a Partially Wetting Film Down a Vertical, Flat Plate," A.H. Liu, P.C. Wayner, Jr., and J.L. Plawsky, AIChE 1995 Annual Meeting, November 12-17, Miami Beach, FL.

PR16) "Film Drainage on a Vertical Surface," A.H. Liu, P.C. Wayner, Jr., and J.L. Plawsky, 1996 Annual Meeting of the ACS, New Orleans, LA, March 24-28, 1996.

PR17) P 17 above

PR18) Nitta, S., Gill, W. N., Wayner, P.C. Jr., and J.L. Plawsky, "Ellipsometric Characterization of Silica-based Aerogels for Interlayer Dielectric" Presented at 1997 Annual meeting of AIChE, New Orleans, LA, Nov. 17-21.

PR19) P 19 above and DOE/ER/14045-13 below

PR20) "Spin-on Xerogel Films for Deep Submicron Devices", Jain, A., Pisupatti, V., Nitta, S., Gill, W. N., Wayner, P.C. Jr., and J.L. Plawsky, Accepted for presentation at TechCon 1998, Las Vegas, Nevada, September 9-11.

DOE REPORTS

DOE/ER/14045-1) "Microcomputer Enhanced Optical Investigation of Spreading and Evaporative Processes in Ultra Thin Films", P.C. Wayner, Jr., M. Sujamani and A.H. Liu, DOE Progress Report DOE/ER/14045-1, January 1990.

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DOE/ER/14045-2) "Microcomputer Enhanced Optical Investigation of Spreading and Evaporative Processes in Ultra Thin Films", P.C. Wayner, Jr., M. Sujanani and A.H. Liu, DOE Progress Report DOE/ER/14045-2, December 1990.

DOE/ER/14045-3) P3 above

DOE/ER/14045-4) P5a & P5b above

DOE/ER/14045-5) "Microcomputer Enhanced Optical Investigation of Spreading and Evaporative Processes in Ultra Thin Films", P.C. Wayner, Jr. and A.H. Liu, DOE Progress Report DOE/ER/14045-5, December 1991.

DOE/ER/14045-6) P8 above

DOE/ER/14045-7 "Microcomputer Enhanced Optical Investigation of Spreading and Evaporative Processes in Ultra Thin Films", P.C. Wayner, Jr., DOE Progress Report DOE/ER/14045-7, January 1993.

DOE/ER/14045-8) P12 above

DOE/ER/14045-9) , P.C. Wayner, Jr. and J.L. Plawsky, "Development and Use of Image Scanning Ellipsometer to Study the Dynamics of Heated Thin Liquid Films", DOE Progress Report DOE/ER/14045-9, January 1994.

DOE/ER/14045-10) , P.C. Wayner, Jr. and J.L. Plawsky, "Development and Use of Image Scanning Ellipsometer to Study the Dynamics of Heated Thin Liquid Films", DOE Progress Report DOE/ER/14045-10, January 1995.

DOE/ER/14045-11) , P.C. Wayner, Jr. and J.L. Plawsky, "Development and Use of Image Scanning Ellipsometer to Study the Dynamics of Heated Thin Liquid Films", DOE Progress Report DOE/ER/14045-11, January 1996.

DOE/ER/14045-12) , P.C. Wayner, Jr. and J.L. Plawsky, "Development and Use of Image Scanning Ellipsometer to Study the Dynamics of Heated Thin Liquid Films", DOE Progress Report DOE/ER/14045-12, January 1997.

DOE/ER/14045-13) same as P19

DOE/ER/14045-14) , P.C. Wayner, Jr. and J.L. Plawsky, "Development and Use of Image Scanning Ellipsometer to Study the Dynamics of Heated Thin Liquid Films", DOE Final Report DOE/ER/14045-14, July 1998.

DISCLOSURE OF INVENTION

Image Scanning Ellipsometer (ISE), to Dr. Chris LeMaistre, Head, Patent & Licensing at Rensselaer Polytechnic Institute, September 18, 1992. After a patent search through the Patents and Licensing Department at RPI, it was decided that an application for the above invention would be rejected (in their opinion) on the basis of anticipation and/or obviousness. Nonetheless, the ISE has many uses.