4ar Interfacial Effects and Properties of Ultrathin Polymer Films: from Nanofabrication to Large-Area Displays

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Polymeric materials play a crucial role in many diverse electronics applications, ranging from advanced nanofabrication (photoresists) to new large-area, flexible displays (conjugated electroactive polymers). Although these polymers vary tremendously in structure and function, many of these applications employ polymers in thin films or at interfaces where the local structure and changes in properties greatly affect their performance. These nanoscale phenomena are investigated using several powerful measurement methods including neutron reflectivity, x-ray reflectivity, small angle neutron scattering, quartz crystal microbalance, and atomic force microscopy. Here, we study and investigate fundamental issues of interfacial effects in microelectronics and organic electronics.

Resolution Limits of Next-Generation Photoresists To maintain Moore's law and increase microprocessor performance, the microelectronics industry requires smaller critical dimensions of the devices with ever sophisticated nanofabrication methods. A grand challenge for this technology is reducing / controlling line edge roughness (LER) in the advanced resists to less than 2 nm. LER can be controlled to a finite level by increasing the optical quality of the latent image, however this finite level is fast approaching the maximum acceptable LER. Identifying the material sources of LER is a complex problem because of the multitude of potential contributions such as the physical properties of ultrathin resist films and the spatial form of the key reaction-diffusion process that creates a latent image upon exposure. The relationship between interfacial width of the latent image and LER is explored using a model bilayer approach to simulate the line edge. The influence of each resist component is systematically examined through a combination of neutron and x-ray reflectivity, FTIR spectroscopy, and AFM. Measurements of these interfacial deprotection profiles provide a fundamental understanding of the material origins of LER and may lead to strategies to minimize LER for future technology nodes.

Selected publications:

- Prabhu, V.M.; Vogt, B.D.; Wu, W.-l.; Douglas, J.F..; Lin, E.K.; Satija, S.K.; Goldfarb, D.L.; Ito, H. “Interfacial structure of photoresist thin films in developer solutions.” *Proc. SPIE*, **2005**, 5753-34.
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- Schmid, G. M.; Stewart, M. D.; Wang, C. –Y.; Vogt, B. D.; Prabhu, V. M.; Lin, E. K.; Willson, C. G. “Resolution limitations in chemically amplified photoresist systems.” *Proc. SPIE*, **2004**,5376-34.
- Prabhu, V. M.; Wang, M. X.; Jablonski, E. L.; Vogt, B. D.; Lin, E. K.; Wu, W. L.; Goldfarb, D. L.; Angelopoulos, M.; Ito, H. “Fundamentals of Developer-Resist Interactions for Line-Edge Roughness and CD control in Model 248 nm and 157 nm Photoresists” *Proc. SPIE*, **2004**, 5376-47.

Small Molecule Diffusion into Ultrathin Polymer Films Further, the thickness of the photoresist films used to pattern nanoscale features is rapidly decreasing, particularly for the anticipated adoption of EUV lithography. For ultrathin films (< 40 nm), it has been shown that the dynamics of several crucial processes become film thickness dependent – moisture uptake, dissolution rate, and acid diffusion. These processes are measured using complimentary techniques of quartz crystal microbalance, x-ray reflectivity, and neutron reflectivity. To garner a fundamental understanding of the origins of this thickness dependent behavior, the moisture uptake in thin films is examined systematically, exploring the influence of film thickness, surface chemistry, and polymer hydrophilicity. These measurements provide fundamental understanding of moisture transport in ultrathin polymer films, which can be extended to predict other dynamic processes in thin films.

Selected publications:

- B.D. Vogt, C.L. Soles, H.-J. Lee, E.K. Lin, W.-l. Wu. "Substrate influence on moisture absorption into thin poly(vinyl pyrrolidone) films." *Polymer* **2005** 46(5) 1635-1642.
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- B.D. Vogt, C.L. Soles, R.L. Jones, C.-Y. Wang, E.K. Lin, W.-l Wu, S.K. Satija, D.L. Goldfarb, M. Angelopoulos. "Interfacial effects on moisture absorption in thin polymer films." *Langmuir* **2004** 20(13) 5285-5290.
- B.D. Vogt, C.L. Soles, H.-J. Lee, E.K. Lin, W.-l. Wu. "Moisture Absorption and Absorption Kinetics in Polyelectrolyte Films: Influence of Film Thickness." *Langmuir* **2004** 20(4) 1453-1458.
- Soles, C. L.; Vogt, B. D.; Jones, R. L.; Prabhu, V. M.; Wu, W. L.; Lin, E. K.; Goldfarb, D. L.; Angelopoulos, M. "Dynamics, Diffusion, and Dissolution in Ultrathin Photoresist Films" Advances in Imaging Materials and Processes, *Proceedings of the 13th International Conference on Photopolymers*, Mid-Hudson Section of Society of Plastics Engineers, Brookfield, CT, **2004**.

Multilayer Moisture Barrier Layers for Large-Area, Flexible Displays Moisture is also a key impediment to the commercialization of flexible organic displays. Water degrades the active material in the organic light emitting device (OLED). Transparent, flexible moisture permeation barriers are necessary to achieve reasonable device lifetimes. Multi-layered barrier materials have shown great promise, but the mechanism behind their effectiveness has been elusive and the quantification of the very low moisture permeation rates has been exceedingly difficult. Using neutron and x-ray reflectivity measurements within a controlled environment, we show that moisture accumulation at the organic/inorganic interfaces in these multi-layered barriers is responsible for the long lifetime of devices using this encapsulation rather than any intrinsic decrease in the transport properties of water within the barrier material. This understanding of the mechanism allows for new strategies for further improving OLED lifetime by encapsulation in multi-layered barriers.

Selected publications:

- E.P. O'Brien, C.C. White, B.D. Vogt "Correlating Interfacial Moisture Content and Adhesive Fracture Energy of Polymer Coatings on Different Surfaces" submitted to Advanced Engineering Materials.
- B.D. Vogt, H.-J. Lee, V.M. Prabhu, D.M. DeLongchamp, S.K. Satija, E.K. Lin, W.-l. Wu. "X-ray and neutron reflectivity measurements of moisture transport through model multilayered barrier films for flexible display applications." *Journal of Applied Physics* **2005** 97(11) 114509..
- B.D. Vogt, V.M. Prabhu, C.L. Soles, S.K. Satija, E.K. Lin, W.-l. Wu. "Control of moisture at buried polymer / alumina interfaces through substrate surface modification." *Langmuir* **2005** 21(6) 2460-2464.