MICRO
DEFECT REDUCTION AND YIELD ENHANCEMENT STRATEGIES
FOR SEMICONDUCTOR AND ADVANCED MICROELECTRONICS

Evaluating the impact of an acetylenic diol–type surfactant on DUV lithography performance

Peng Zhang, Danielle M. King, and Eugene J. Karwacki,

Air Products and Chemicals

Lithography is the key enabling process for the manufacture of integrated circuits. The newly updated *International Technology Roadmap for Semiconductors* shows that by 2004, critical features, as measured by the gate length of MPUs and the half-pitch of DRAM devices, will break the 100-nm barrier.[1] Paralleling the reduction in line geometries is the need to tighten control over the lithographic process. Critical dimension (CD) is a closely monitored process control lever. At the 90-nm technology node, CD control, as measured by the 3σ requirement, will approach 3.0 nm, which is close to the size of the polymer molecules that comprise photoresist. Furthermore, this level of precision will have to be achieved on 300-mm wafers. Accomplishing this level of control will challenge all the processes that lithography encompasses: photoresist, exposure, development, and metrology.

Experiments show that an acetylenic diol–type surfactant in photoresist developer improves the wetting of the developer on DUV resist surfaces, leading to faster and more-uniform development.

One approach to addressing the need for tighter CD control is to improve the development process. This approach makes sense, since advanced photoresists for 193-nm lithography will be more aliphatic and, consequently, more resistant to developer wetting than the resists used in earlier lithography generations. In 193-nm lithography, poor wetting of the photoresist by the developer will possibly lead to reduced CD control and postdevelopment defects. It is

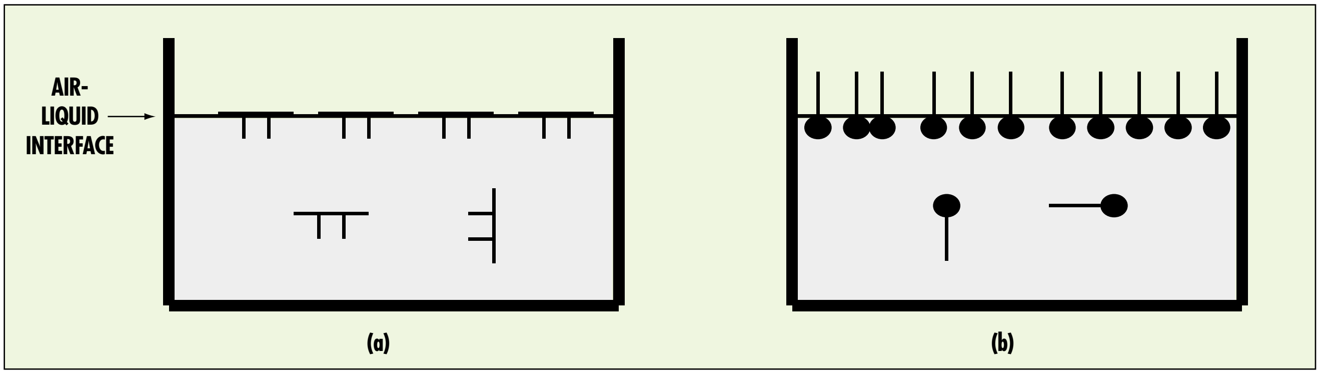

Figure 1: Schematic drawings showing the molecular packing of (a) acetylenic diol–type surfactants and (b) alcohol ethoxylate surfactants at the air/liquid interface.

anticipated that these problems will be further magnified with the transition to 300-mm processing, because greater surface area will have to be wetted during the same time period.

One method used to ensure rapid and uniform wetting is to mix a surfactant into the developer.[2] However, some classes of surfactants have the unfortunate side effect of foaming or forming microbubbles, which may generate defects and decrease yields, especially during contact-hole printing. Surfynol, a class of Gemini surfactants from Air Products and Chemicals (Allentown, PA) with an acetylenic diol–type structure, is used extensively in applications where dynamic wetting and low foaming are critical performance metrics for rapid surface wetting.[3] With these characteristics, Surfynol surfactants, when incorporated into tetramethyl ammonium hydroxide (TMAH) photoresist developer, can help improve CD control and reduce defect levels.

This article discusses a study that was conducted to investigate the fundamental behavior of developers formulated with the acetylenic diol–type surfactant and evaluates the impact of using this class of surfactant in a 248-nm DUV lithography process.

Experimental Procedure

The DUV resist was coated on 200-mm silicon wafers covered with an organic antireflective coating. The film was exposed using a /300B D4576 stepper from ASML (Veldhoven, The Netherlands) interfaced with a Polaris 2100 microlithography tool from FSI International (Chaska, MN). The illumination mode was quadrupole, with NA of 0.63, a σ_{inner} of 0.5, and a σ_{outer} of 0.8. The softbake and postexposure temperatures were each set at 110°C for 60 seconds. Using three different loading processes—low, medium, and high—the acetylenic diol–type surfactant was added to Air Products' 0.26-N TMAH developer to form three enhanced formulations (A, B, and C). The film was developed using a 60-second single-puddle process followed by a DI-water rinse.

The wettability of each developer was evaluated using drop-shape analysis developed by Krüss (Hamburg, Germany), which measures the contact angle of a droplet on the resist-coated wafer surface. A high-speed camera captured the spreading of the droplet at a speed of 2 frames/sec. Contact angles were measured on both unexposed and exposed resist surfaces.

The dynamic surface ten-

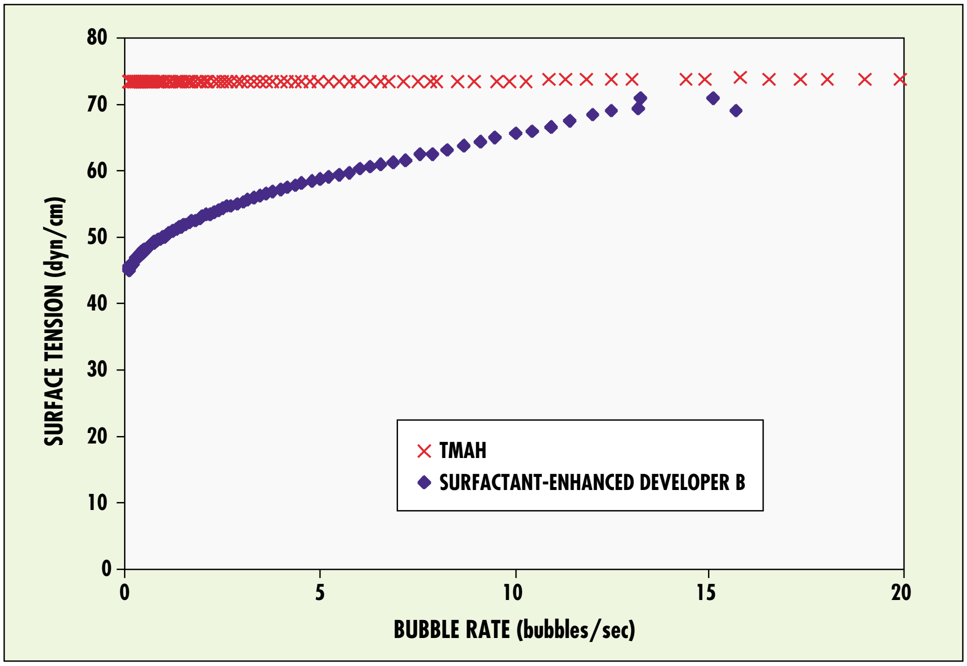

Figure 2: Surface tension of pure TMAH and the developer with acetylenic diol–type surfactant measured at different bubble rates. High bubble rates represent faster generation of new surface and more-dynamic conditions.

sion of each developer was characterized using a Krüss maximum-bubble-pressure tensiometer with a 0.28-mm-diam capillary tube lowered to a depth of 10 mm. As nitrogen blew through the capillary into the developer solution at a high bubble rate, new air/liquid interfaces were generated quickly. Measurements were taken at intervals of approximately 20 bubbles/sec to 0.1 bubble/sec.

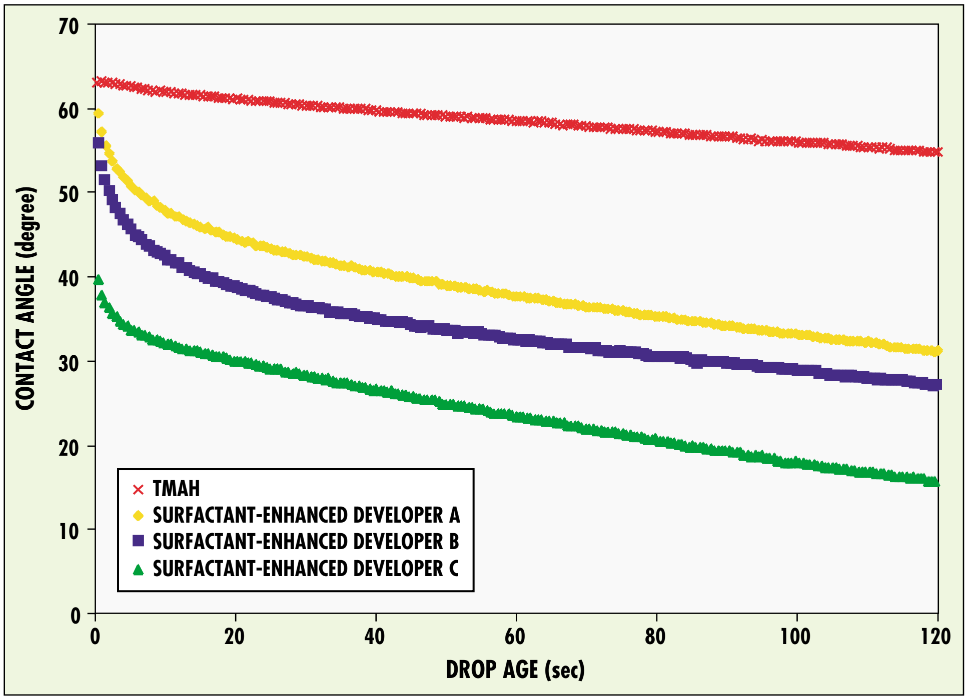

Figure 3: Contact angles of droplets of TMAH and the developer with acetylenic diol–type surfactant on unexposed DUV resist–coated wafer surfaces, captured by a high-speed camera.

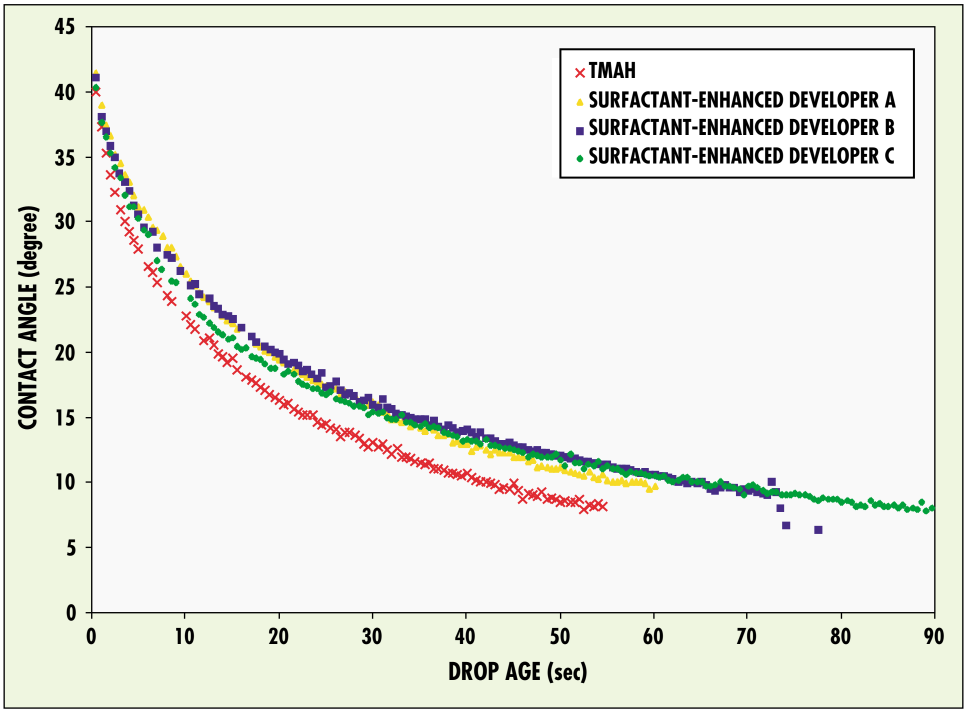

Figure 4: Contact angles of developer droplets of TMAH and the developer with acetylenic diol–type surfactant on exposed DUV resist–coated wafer surfaces.

Surface Activity

Typically, the ability to reduce surface tension translates directly into enhanced substrate wetting and coverage. It also leads to a more-uniform distribution of developer. Equilibrium surface tension is important when a system is at rest. However, the ability to reduce surface tension under dynamic conditions is of great importance in applications where surfaces are being generated. The process of dispensing the developer onto the wafer, having it contact the resist surface, and spreading it across the wafer is a dynamic wetting process.

Traditional nonionic surfactants such as alkylphenol or alcohol ethoxylates and ethylene oxide/propylene oxide copolymers offer excellent equilibrium surface tension, but they are generally characterized as offering poor dynamic wetting. In comparison, surfactants based on acetylenic glycols are known for their ability to lower both equilibrium and dynamic surface tension.

Figure 1 illustrates the difference in the molecular packing at the air-liquid interface between a typical nonionic surfactant and an acetylenic diol–type surfactant. While typical nonionic surfactants with a single head-tail structure pack efficiently at the air-liquid interface to reduce the equilibrium surface tension, the bulky molecules of acetylenic diol–type surfactant exhibit superior dynamic properties because of their relatively high bulk concentration, which results from inefficient molecular packing at the air/liquid interface.

The differences in dynamic surface tension between pure TMAH developer and the developer containing acetylenic

Developer Formulation	150-nm Dense Lines		180-nm Contact Holes	
	CD (nm)	3σ (nm)	CD (nm)	3σ (nm)
Pure TMAH	141.3	6.7	183.3	13.0
Enhanced developer A	136.0	4.9	186.8	8.1
Enhanced developer B	135.0	8.3	189.6	9.1
Enhanced developer C	132.0	7.3	190.6	11.3

Table I: Mean CD and CD uniformity data for pure TMAH developer and for the developer with the acetylenic diol–type surfactant under three different loading conditions.

diol–type surfactant added under medium loading conditions are presented in Figure 2. At a high nitrogen-bubble rate, new surfaces are generated quickly, which creates a dynamic situation. Acetylenic diol–type surfactant steadily lowers the surface tension of the solution under such conditions. For developer formulations without the surfactant, the surface tension remains the same under both static and dynamic conditions.

Wetting Characteristics

Figure 3 shows the contact angles of developers with and without surfactant as a function of development time on unexposed DUV resist. The figure compares the performance of pure TMAH with the developer containing acetylenic diol–type surfactant added under all three loading conditions. The developer formulations containing the surfactant had smaller contact angles than the developer without the surfactant, indicating that the use of the surfactant improves resist-surface wetting. Moreover, high surfactant loading produced a smaller contact angle than low surfactant loading, indicating that high loading causes the wafer surface to become wet faster.

Figure 4 shows the contact angles of developers with and without surfactant as a function of development time on exposed DUV resist. The acid generated during exposure unblocked the acid-protective groups on the polymer backbone. As a result, the polymer became soluble in base and much more hydrophilic in nature. The contact angles of all three developer formulations were therefore smaller on exposed resist than on unexposed resist, indicating that the exposed resist dissolves faster in the developer. Although the high dissolution rate made it difficult to differentiate between the wetting behavior of the different developer formulations, it could be assumed that high surfactant loading causes the wafer surface to become wetter faster than does low surfactant loading, as in the case of the unexposed resist.

DUV Performance

The study assessed the impact of acetylenic diol–type surfactant on 150-nm dense lines and 180-nm contact holes in a DUV development process. Mean CD values and CD uniformity data are summarized in Table I. Figures 5a and 5b show cross-sectional SEM profiles of 150-nm dense lines developed using pure TMAH and surfactant-enhanced developer A, respectively, while Figures 6a and 6b show cross-sectional SEM profiles of 180-nm dense contact holes developed using pure TMAH and surfactant-enhanced developer A, respectively. As can be seen in the images, the presence of surfactant had no obvious impact on feature profiles.

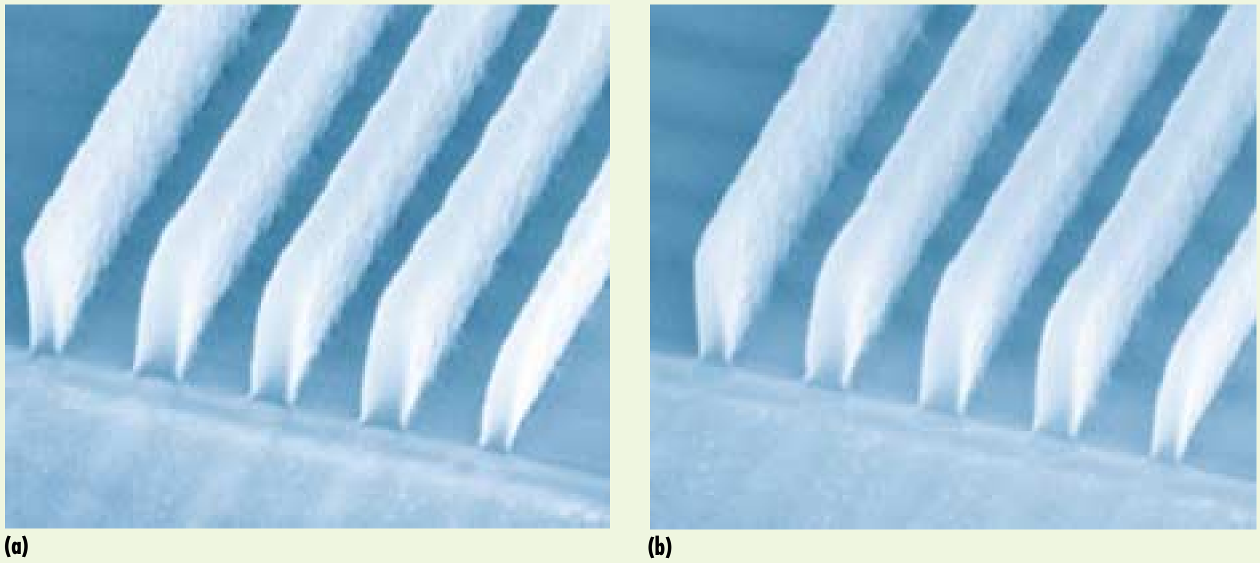

Figure 5: Cross-sectional SEM images of 150-nm dense lines developed by (a) TMAH developer and (b) the developer with acetylenic diol–type surfactant.

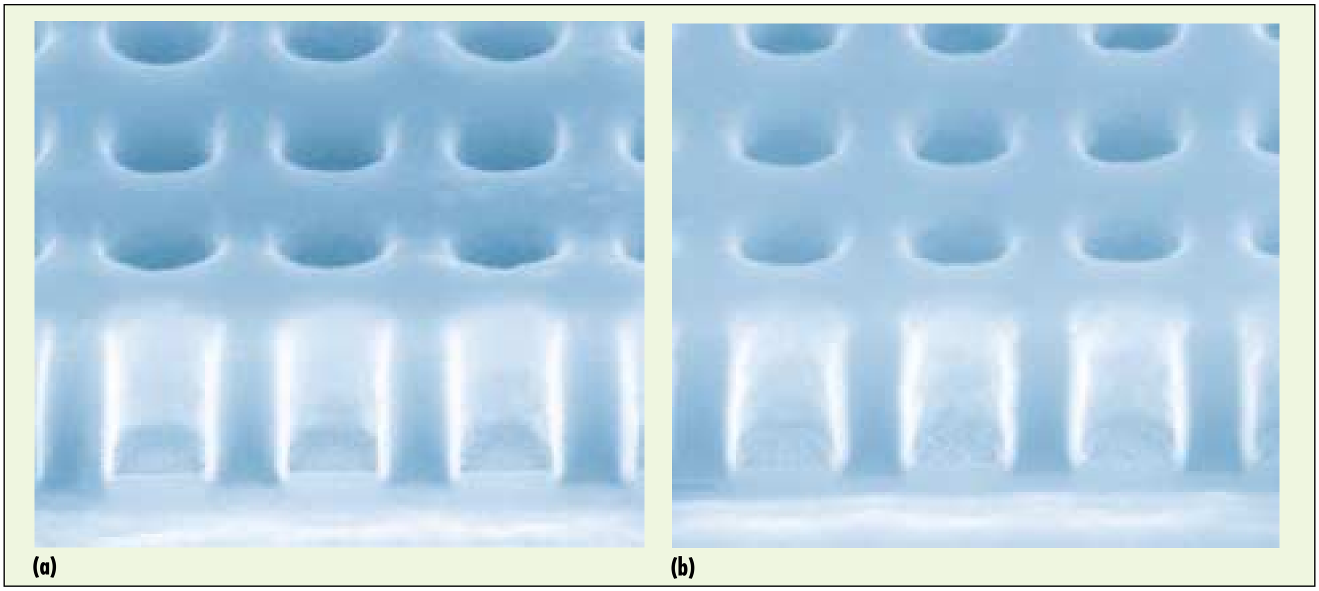

Figure 6: Cross-sectional SEM images of 180-nm dense contact holes developed by (a) TMAH and (b) the developer with acetylenic diol–type surfactant.

As surfactant loading increased, however, the CD values decreased for the dense lines but increased for the contact holes. The presence of surfactant may have contributed to faster development rates caused by the improved wetting on the resist surface. Consequently, the use of a surfactant may make it possible to improve equipment throughput by shortening development times or lowering exposure doses.

Another advantage of using surfactant is that it results in a significant improvement in CD uniformity. The 3σ value of the 150-nm lines developed with surfactant-enhanced developer A was 27% lower than the 3σ value of the lines developed with pure TMAH, while the 3σ value of the 180-nm contact holes developed with surfactant-enhanced developer A was 37% lower than the 3σ value of the holes developed with pure TMAH. This improvement was likely the result of the increased wetting that takes place when TMAH is mixed with the surfactant. As shown in Table I, improved wetting has a greater impact on the CD uniformity of contact holes than on the CD uniformity of lines and spaces because it is more difficult to wet the inner walls of contact holes than lines and spaces. The data also suggest that the level of surfactant loading affects CD performance. Optimizing the developer formulation is important to achieve the best CD control.

The data presented in Table II indicate that the presence of surfactant has little impact on depth of focus (DOF). However, the use of the surfactant caused the exposure latitude (E_{lat}) to fall slightly. Typically, exposure latitude is a performance parameter that requires high dose control. Contact-angle data show that the use of the enhanced developer formulation resulted in better wetting on unexposed resist surfaces than on exposed ones, resulting in a slight decrease in contrast. This may explain the exposure latitude reduction.

Conclusion

Experiments revealed that an acetylenic diol–type surfactant in a TMAH-based photoresist developer improved the wetting of the developer on DUV resist surfaces. The resulting improvement in mean CD values, particularly for dense lines, and in CD uniformity, particularly for contact holes, indicates that faster development rates and more-uniform development can be achieved by using the surfactant. Also, surfactant loading was found to have an important impact on CD performance. Thus, optimizing developer formulations enables fabs to increase equipment throughput and yields.

Developer Formulation	150-nm Lines		180-nm Contact Holes	
	DOF (µm) (10% E_{lat})	E_{lat} (%) (0.6-µm DOF)	DOF (µm) (10% E_{lat})	E_{lat} (%) (0.6-µm DOF)
Pure TMAH	1.2	15.0	1.1	21.7
Enhanced developer A	1.2	14.3	1.1	20.8
Enhanced developer B	1.2	13.3	1.1	19.1
Enhanced developer C	1.1	13.6	1.1	20.7

Table II: Depth-of-focus and exposure latitude data for pure TMAH developer and for the developer with the acetylenic diol–type surfactant under three different loading conditions.

Acknowledgments

The authors thank Chris Smith of Motorola, Mordy Rothschild and Dave Astolfi of the Massachusetts Institute of Technology's Lincoln Laboratory, and ASML's demonstration facility in Tempe, AZ, for their invaluable input and support in obtaining the DUV data used in this article.

References

1. *The International Technology Roadmap for Semiconductors*, Lithography section (San Jose: Semiconductor Industry Association, 2001).
2. H Shimada et al., "Residual-Surfactant-Free Photoresist Development Process," *Journal of the Electrochemical Society* 139, no. 6 (1992): 1721–1730.
3. J Schwartz, "The Importance of Low Dynamic Surface Tension in Waterborne Coatings," *Journal of Coating Technology* 64, no. 812 (1992): 65–74.

Peng Zhang, PhD, is a principal research chemist in the electronics technology department of Air Products and Chemicals (Allentown, PA), where she works on product development and applications support for photoresist developers. Her research focus at the company has been in the area of surfactant technology in electronics-related applications. She received a BS in chemistry from Peking University in Beijing and a PhD in organic chemistry from the University of Illinois at Urbana-Champaign. (Zhang can be reached at 610/481-3576 or zhangp2@apci.com.)

Danielle M. King is an applications engineer in the semiconductor processing applications group at Air Products and Chemicals, where she has been for 3½ years. She received a BS in chemical engineering from the University of Florida in Gainesville. (King can be reached at 610/481-4201 or kingdm@apci.com.)

Eugene J. Karwacki, PhD, is a senior research associate and the research manager for semiconductor processing applications in the electronics division of Air Products and Chemicals. He joined the company in 1982 as a member of the corporate analytical staff. He has worked in various technical positions at the company in research and operations. His research group is focused on developing new products and applications for dielectric materials, etching gases, chamber cleaning, and photoresist ancillaries. Karwacki has published more than 35 papers and holds two patents. He received a BS in chemistry from Loyola College in Baltimore and a PhD in chemistry from Pennsylvania State University in State College. (Karwacki can be reached at 610/481-5934 or karwacej@apci.com.)

Reprinted from *MICRO* June 2002 • Copyright © 2002 Canon Communications LLC