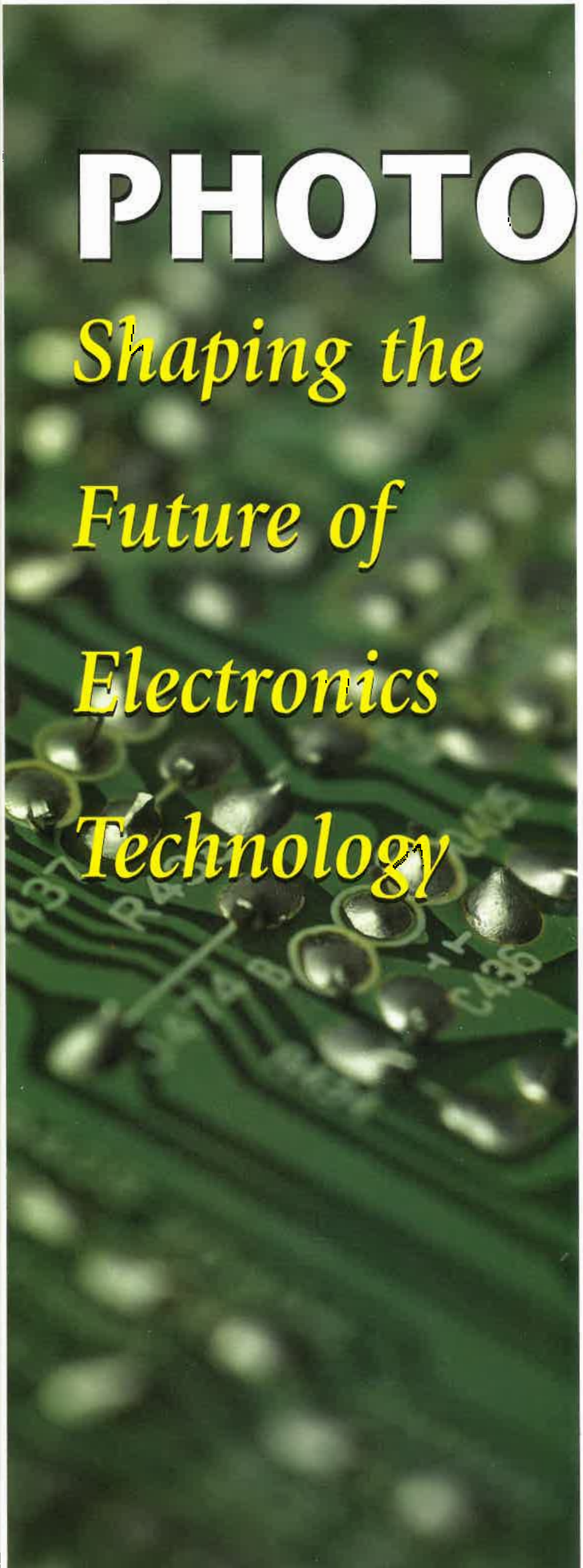
PHOTORESISTS: *Shaping the Future of Electronics Technology*



The advancement of semiconductor technology correlates directly with the ability of photoresist companies to develop products that can be used to pattern circuits on silicon wafers at ever smaller dimensions. Polymer composition has changed as new technology nodes have been approached and surpassed. Interest in silicon-based polymers is growing as the limits of organic polymer technology are reached. The need for antireflective coatings has also grown as circuit size has diminished. Immersion photolithography, the latest technology adopted by the semiconductor industry, now presents additional challenges to photoresist producers.

Photoresists contain polymers sensitive to light that are laid down on the silicon wafer (typically spun on). A photomask of the desired circuit pattern positioned three to six feet away from the wafer is used to project an image at 4X reduction onto the wafer surface through a multi-million dollar lens. The uncovered areas of the polymer are exposed to specific patterns of light at a given wavelength, causing chemical and physical changes that make it either soluble in a developer solution (positive tone) or resistant to the developer (negative tone). After the reacted polymer is removed, the wafer not protected by the remaining photoresist is etched to create the integrated circuit pattern. The process is repeated multiple times to create the final chip structure. Most integrated circuits are fabricated using positive tone photoresists.

Metal ion-free developers, which contain only parts per billion of metal ions, are composed largely of deionized water and the base tetra methyl ammonium hydroxide (TMAH). The purity of the developers is critical, as the presence of iron, sodium, potassium, and other metal ions in developers can cause leakage currents in gate oxides, hindering CMOS device performance. The concentration of the TMAH varies depending on the photoresist formulation, and some developers also contain surfactants for improved surface wetting properties.

Once the reacted portion of the polymer is removed, the remaining photoresist serves as a mask for pattern-

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ing the circuits on to the wafer. The ability of the coating to "resist" degradation during the etching step leads to the second part of the name "photoresist." Etching is typically achieved via a dry plasma etching process. The reactive plasma contains ionized oxidizing or reducing agents that react with the exposed surface material, removing them from the substrate. Wet etching, which is an older technology, involves the use of liquid chemicals. Dry etching is preferred because it is generally an anisotropic process, while wet etching is an isotropic process, with the etching occurring in all directions.

After the etching process, the remaining photoresist is removed with a wet chemical solution. A wet-wet process is used for older technology to remove both the photomask and photoresist. For less than 0.50 micron geometries, a dry-wet process that involves the use of a dry oxygen plasma (ashing) to remove the photoresist mask and a wet chemical process for removal of the photoresist residue is typically employed. Wet strippers are often comprised of the polar solvent N-methyl-2 pyrrolidone (NMP) and an alkanolamine such as monethanolamine (MEA). Corrosion inhibitors are sometimes added, or a further rinse with isopropanol used to minimize corrosion by the NMP and MEA. To remove photoresist residue following plasma ashing, aqueous hydroxylamine-based removers have been developed. Alternative wet processes are being investigated in order to eliminate the plasma ashing step.

Several different polymer types have been utilized in photoresist formulations over the years. The chemical makeup of the polymers has changed to adjust the sensitivity to shorter wavelengths of light. "A functional difference between these polymers is the absorbance or transmittance of light by the polymer in the photoresist formulation. The polymer must allow the imaging light to transmit through the photoresist," comments Dr. Matthew Romberger, manager, sales and marketing, with DuPont Electronic Polymers.

According to Kathryn Durham, marketing director for AZ Electronic Materials USA, the classic photoresist used by the industry since about 1970 is the DNQ/novolak type. DNQ stands for diazonaphthoquinone, a light-sensitive compound that in its unexposed form interacts with a cresol/formaldehyde resin, the novolak, to make a product that is insoluble in aqueous alkaline developer solution. After exposure to light, the photoproducts of the DNQ enhance the solubility of the coating. "The ratio of the exposed/unexposed dissolution rates can exceed 100,000, which makes it possible to achieve very straight sidewalls," explains Dr. Ralph Dammel, R&D director for AZ Electronic Materials. "In effect, the photoresist acts as a chemical rectifier, turning an aerial image that is near to a sine wave into a square wave." These photoresists are used in "broadband," "G-line," and "I-line" photolithography. Cyclized rubber/bisazide photoresists have also been used in these applications, according to Dr. Romberger.

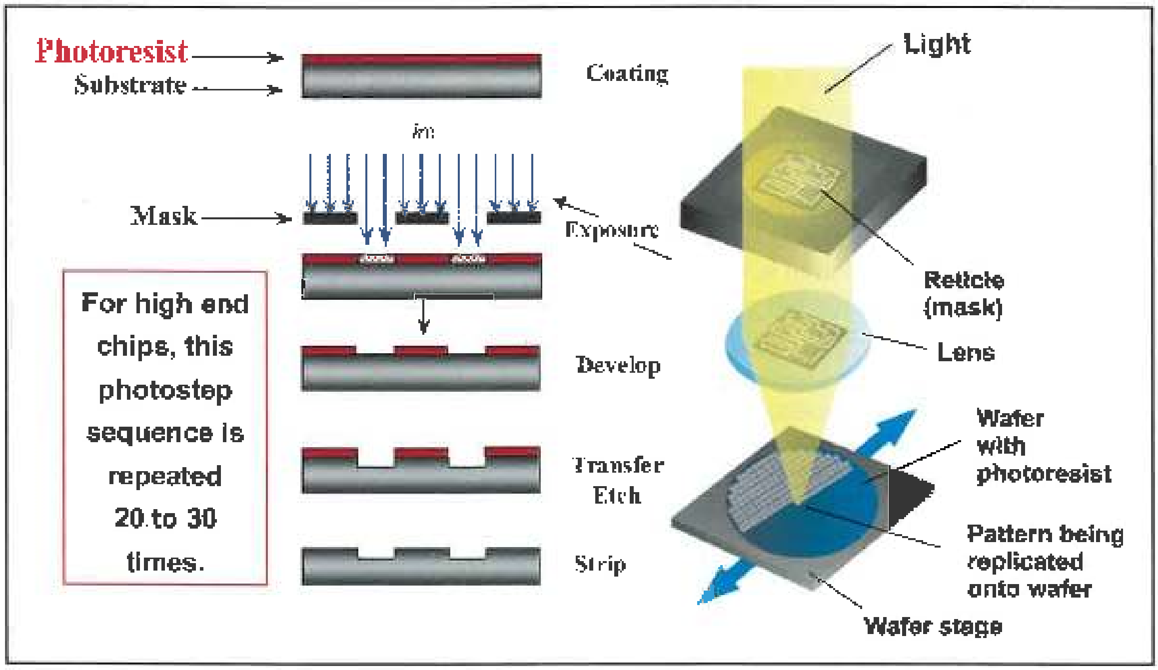
Shorter wavelengths of light have been necessary in order to create smaller and smaller printed features. To achieve better resolution for 248 nm lithography, poly(hydroxystyrene) (PHS), a novolak isomer, has been used as an alternative. The changeover was not simple, however, because DNQs do not inhibit PHS like they do novolak resins. "To overcome this problem, a new imaging scheme called chemical amplification was developed," says Dr. Dammel. Deep ultraviolet (DUV) photoresists started gaining momentum and use in the late 1980s and early 1990s, and became the industry's mainstream solution in 1997. KrF photoresists can be used to make images with resolutions <100 nm.

In one common type of 248 nm resists, about 20% of the hydroxyl groups of PHS are protected with t-butoxycarbonyl (t-BOC) moiety. A photoacid generator (PAG) that releases a strong, non-nucleophilic acid such as triflic acid or a higher homolog upon exposure is mixed into the coating solution. The acid catalyzes the decomposition of the t-BOC group into CO_2 and isobutene; the phenolic OH group is regenerated and the polymer becomes soluble. "Since the acid is a true catalyst and not consumed during the reaction, it can

Selected Photoresist Suppliers

- Air Products and Chemicals, Inc.
- AZ Electronic Materials
- Brewer Science
- Dongjin Semichem Co. Ltd.
- Dong Woo Fine Chemicals
- Dow Corning (resin only)
- DuPont Electronic Polymers (resin only)
- Everlight Chemicals FujiFilm
- JSR Microelectronics Corporation
- Microchem
- Nagase
- Rohm and Haas Electronic Materials
- Shin-Etsu Chemical Company
- Sumitomo Chemical Company
- Tokyo Ohka Kogyo

Source: SEMI®



Photolithographic process. Figure courtesy of AZ Electronic Materials.

go on to de-protect more sites. The initial photo event is thus multiplied by the number of catalyzed reactions, leading to the name of 'chemical amplification' for this imaging scheme. With chemical amplification, photoresist sensitivity is greatly enhanced," said Dr. Dammel. A more recent version of the technology relies on a copolymer of hydroxystyrene and t-butylacrylate known as ESCAP (Environmentally Stable Chemically Amplified Photoresist).

For 193 nm lithography, PHS and all aromatic systems are too absorbing to allow for sufficient transmission of light necessary for imaging. Aliphatic resins, however, exhibit poor dry etch resistance. "To overcome this difficulty, the industry developed photoresists based on highly fused ring systems, such as adamantane methacrylates, that contain a high carbon content," said Dr. Dammel. According to Ms. Durham, today most systems use cleavable 2-alkyl-2-adamantane methacrylate copolymerized with lactone and fused ring alcohols in order to offset the high hydrophobicity of the adamantane ring. These ArF photoresists were introduced in the late 1990s and early 2000s. These newer ArF materials can resolve to 32 nm or better.

The use of antireflective coatings (ARCs) has also become critical to the patterning process as size has continued to decrease. "Antireflective coatings are used to eliminate reflection and interference effects that otherwise would degrade the ability of the photoresist to print fine patterns true to the intended shape," states Dr. Dammel. The reflective nature of polysilicon, aluminum and copper films, photoresist thicknesses, and device topography can all affect the path that light travels. ARCs applied to either the top of the photoresist (TARCs) or bottom (BARCs) have become common place. TARCs are easier to apply and to remove and limit the effects of variations in photoresist thickness, but do not suppress reflections resulting from device topography. BARCs help eliminate all types of unwanted reflections, but add cost and complexity due to the additional application and removal processes required. Today, most 248 nm and basically all 193 nm processes use bottom antireflective layers (either inorganic or organic layers applied by CVD or q spin on process) as a matter of course.

Final photoresist formulations include the resin, photo acid generator, adhesion promoters, solvent blends for spinnability, and the resin (or perhaps a blend of resins). Photoresist producers differentiate their products in a number of ways. Many photoresists are custom produced to meet specific needs of customers. Modifications are incorporated to the basic resin structure to make the photoresist more or less sensitive to light, impart a wider optical window of reactivity; increase recoverability; or address purity, shelf life, stability, and other such issues.

Quality of materials is critical. "At DuPont Electric Polymers, we focus on lot-to lot and batch-to-batch reproducibility," says Dr. Romberger. "Once a product or process is approved for semiconductor manufacturing, you want absolute product consistency from that point on. A consistent polymer is key to our customers, and critical to quality photoresists," he stresses. Dr. Dammel adds that "over 80% of problems caused by photoresist variations can be traced to raw material variation. Each variation can be very expensive, since lack of a performing photoresist may completely shut down a multi-billion dollar fabricator."

The market for photoresist and ancillary materials is growing at a healthy rate as semiconductor technology continues to advance. According to SEMI®, an industry organization that represents the semiconductor equipment and materials industry, the value of the global photoresist market for semiconductor use totaled approximately $950 million in 2005. Negative tone resists accounted for just $7 million. The dollar value was split evenly between older technologies and advanced lithography (248 nm–193 nm). By 2007, SEMI expects the market to be worth $1.254 billion, with advanced lithography accounting for 63% of the total. According to DuPont, the market for TFT photoresists used in the production of LCD displays is about $600 million. There are also dry film resists for printed circuit boards (PCBs) and photoresist materials for flat panel displays. These materials are not covered in this discussion.

The developer market experienced a strong downturn in 2001 and 2003 and has not yet recovered the peak volumes experienced prior to that. Efforts to minimize waste through smaller dispense volumes and single wafer processing tools, combined with continued pricing pressures, have kept the numbers down. The fastest growing market for photoresist developers is outside of Japan and North America, where more fabricators are beginning production. Developers in general are produced by photoresist manufacturers. In 2004, SEMI valued the global developer market at $172 million.

After significant declines at the beginning of the decade, the market for removal products has grown over the last three years. In 2004, the global removal market grew by 22%, reaching a value of $360 million. Traditional organic removal materials (NMP-based technologies) are mature but remain cost-effective. Advanced removal materials are experiencing the greatest growth. Companies supplying removal materials include photoresist manufacturers, electronic chemical producers, and specialty chemical companies.

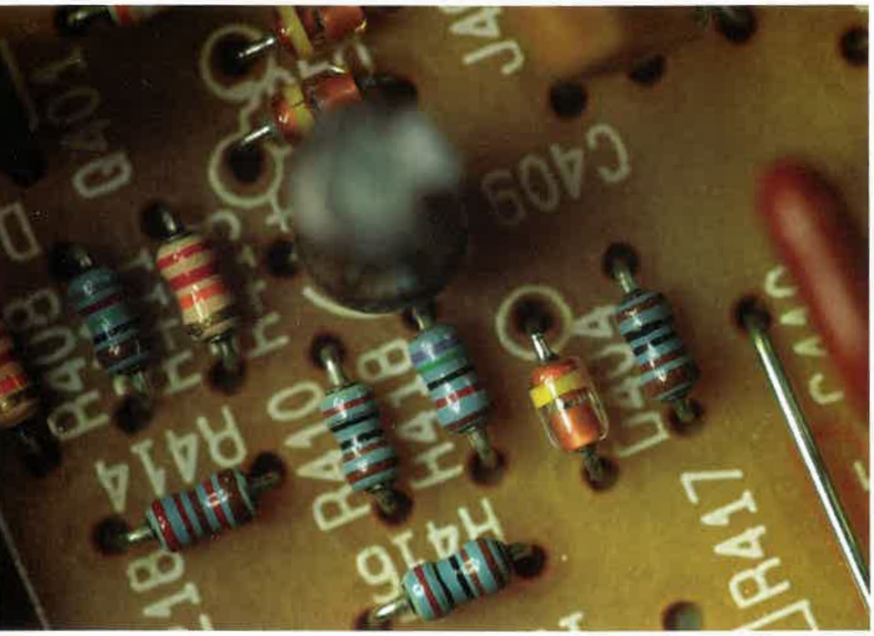
The demand for antireflective coatings has been strong and is expected to remain so as semiconductor fabrication moves to increasingly smaller dimensions. According to SEMI, in 2004 the global ARC market grew 22% to reach a record value of $178 million. Most suppliers of ARCs are photoresist producers, and they tend to produce ARCs compatible with their own photoresist materials. Brewer Science and Honeywell Electronic Materials also manufacture ARCs for use with a wide variety of photoresists from different manufacturers.

As the market and technology has changed over the past two decades, significant consolidation has occurred among photoresist suppliers. Manufacturers face high research and development costs as well as long product development and life cycles. Risk can be significant and customer requirements can be demanding. "No one has the resources to do everything for everybody, though, so we have to sometimes make tough decisions," comments Ms. Durham. "One problem is that some of the further-out technologies require extensive platform development, and even in the case of success a break-even point for such a project may be more than a decade away. This makes it difficult for the materials suppliers to justify heavy investment in such projects."

Photoresist manufacturers' along with the rest of the semiconductor industry, are committed to both developing and following the International Technology Roadmap for Semiconductors (ITRS, www.itrs.net). A volunteer consortium of industry representatives works on the ITRS. It is updated each year, and fully revised every two years, according to Phil Dembowski, global market manager for Semiconductor Fabrication Materials at Dow Corning. Suppliers usually set their timelines and targets according to the ITRS while also considering specific customer inputs and requirements, at least for the nodes closer in time, Ms. Durham adds.

Currently, the semiconductor industry is involved in scaling up existing formulation for the 65 nm technology node, with research and development efforts focused on 45 nm node materials using 193 nm immersion lithography. "Photoresist design and improvement as well as the development of more complex antireflective coatings (dual antireflection layers or trilayer schemes using a silicon-containing BARC and a carbon-rich hardmask, for example) are the focus of much effort," says Dr. Dammel. Work on the 45 nm node should be completed in 2009–2010, and the 32 nm

AZ Electronic Modern Wafer Scan. Photo courtesy of AZ Electronic Materials.



node should be reached by 2012. "Optical lithography using 193 nm immersion technology should enable fabrication of devices down to the 32 nm technology node. After that, an extreme ultraviolet (EUV) light source at 13.5 nm will likely be required. The equipment and photoresists for this technology will be very different," Mr. Dembowski notes. And there are significant challenges to be overcome. "It is possible that a further extension of 193 nm immersion lithography with new, high refractive index liquids and/or double exposure patterning will be used instead of EUV," proposes Dr. Dammel.

Immersion lithography replaces the air gap between the lens of the lithography stepper equipment and the silicon wafer with a higher refractive index material. It is attractive because much of the existing infrastructure, tools, and materials can be utilized. The air gap is a source of limitation for traditional optical lithography because of the refractive index of the air. High purity water has been the initial choice, with a continuously refreshed droplet of water filling the gap. "The light path travels through water, effectively increasing the numerical aperture and therefore enabling a higher resolution and smaller critical dimensions," explains Dr. Romberger. The overall result is that the effective wavelength is lowered to about 132 nm. At the same time, the photoresists are exposed to water (or potentially an organic liquid), raising several issues.

With immersion lithography, the leaching of resist components during their first contact with water, water absorption by the photoresist, the refinement of protective topcoats, and line-edge roughness and other defect sources must be addressed. Photoresist additives such as acids, quenchers, or contrast-enhancement agents could leach out of the film and possibly contaminate or damage the lens. While fabricators would prefer to avoid additional process steps, the application of a protective topcoat may be necessary to alleviate this concern. The removal process must be carefully completed so as not to impact the image quality. Defects associated with the application and removal of the topcoat, interactions with water, formation of bubbles, and other changes in the system are likely to occur and will need to be resolved as well. On the positive side, topcoats may also help adjust the contact angle, providing post exposure delay protection from airborne contamination.

Beyond immersion lithography, EUV technology poses significant challenges for photoresist manufacturers. With chemical amplification, diffusion of the acid reduces the contrast obtained during the exposure step. Typical diffusion lengths of 40 nm will not be tolerable at the 45 nm and smaller technology nodes. Line-edge or line-width roughness (LER or LWR) will also likely impact the electrical performance of devices at these smaller technology nodes. Unfortunately, reducing diffusion length typically results in increased LER.

Inorganic photoresists and antireflective coatings based on silicon polymers are the likely solution to many of the lithography issues that occur at smaller technology nodes. Unlike organic based materials, which are degraded to some extent by the etching process, silicon polymers offer improved etch resistance. Dow Corning is capitalizing on its expertise in silicon chemistry and its experience in other segments of the electronics industry to develop inorganic photoresists and ARCs designed for the 65 nm and smaller technology nodes. "We are working with multiple lithographic companies and photoresist manufacturers to develop silicon-based resins for future semiconductor needs," says Mr. Dembowksi.

Dow Corning has been investing in its photolithography program for over three years now and has more than 20 people working to develop products it hopes to launch to the market within the next couple of years. "Dow Corning has made a significant investment in this program despite the high level of risk," Mr. Dembowski states. "We have worked to minimize the risk by focusing on the silicon chemistry and collaborating with experts in photoresist formulation and semiconductor fabrication," he continues. The company has established an extensive patent portfolio of silicon-based polymers for use in photoresists and antireflective coatings that are based on silsesquioxane technology. Research has focused on modifying the Si-O backbone with different kinds of functionality to impart light absorbing properties, increase ease of strippability, and enhance other desirable features. Dow Corning will be able to produce the resins in its existing facilities following modifications to manufacturing equipment, according to Mr. Dembowski.

In the meantime, new products are being introduced to improve performance at the current technology node. AZ Electronic Materials has launched several new photoresists and antireflective coatings to the market, according to Ms. Durham. "Our new 193 nm products offer improved line-width roughness (LWR) and an enhanced process window for line/space resists, or side lobe margin for contact hole resists." In the thick film area, AZ has introduced chemical amplification technology that allows customers to use much shorter exposure and development times while at the same time achieving higher aspect ratios.

AZ also has new ARC technologies. The company has launched a PFOS-free TARC that is unique to the market, and is also expanding its line of outgassing-free, high etch rate BARCs. AZ has also developed a proprietary photosensitive approach to developer-soluble BARCs, as well as shrink technologies for chemical post-treatment of contact holes and trenches that reduces their dimensions beyond what can be achieved directly by photolithography. Recently, AZ made major investments in its advanced tool sets in the U.S. and expanded production capacity in Asia with the addition of new plants in Taiwan, Korea, Japan, and, most recently, mainland China.

DuPont Electronic Polymers provides highly engineered polymer materials including derivatives of 4'-hydroxyacetophenone that will enable photoresist manufacturers to keep pace with changing technology. "By controlling or influencing the quality of the polymer, we can influence the quality of the photoresist, and the resulting image quality. DuPont is using proprietary and patented technologies to produce photoresist polymers with controlled architecture to meet advanced lithography needs," states Dr. Romberger. The company has introduced several new polymers for photoresist applications under confidentiality agreements with customers. "DuPont leverages science from across the company on a global scale to provide the best material sets available today for the semiconductor industry, and we will continue to support our customers' needs to manufacture advanced photoresists," he adds.

A determined commitment by the entire industry to follow the International Technology Roadmap for Semiconductors has led to significant advances in photoresist and related technology for many years. Despite the significant challenges that lie ahead, both resin producers and photoresist manufacturers will no doubt find solutions to advance semiconductor technology that go well beyond the 32 nm node. Whatever approaches are taken, it is likely that photoresists and antireflective coatings will continue to remain critical components of semiconductor fabrication for many years to come. CT