Description and Applications
The AZ 4000 Series photoresists provide unmatched capabilities in applications requiring film thicknesses of 3-50 μm (2 mil).

Typical applications include plasma processes, extreme topography, thin film magnetic heads, power devices, displays, IR arrays, solar cells, contact up-plating for TAB and hybrids, ceramic packaging, etc. The resist can be baked to form a fully cross-linked resin that acts as an excellent dielectric to remain part of a permanent device structure. Features of the AZ 4000 Series resists that make them ideal for these applications are:

- Exceptional transparency which allows 6-15 μm films to be exposed with 200-400 mJ/cm².
- Broad spectral sensitivity - Superior response to exposure sources ranging from 310-436 nm (UV3 and UV4).
- Steep wall profiles - ideal for up-plating.
- Good adhesion in neutral or acidic plating baths.
- Suitable for contact, proximity or projection printing.

Companion Developers
AZ 400K and AZ 421K are the recommended developers for thick films of AZ 4000 Series photoresists. AZ 400K is a buffered potassium based developer that provides the process latitude associated with inorganic developers while minimizing risk associated with mobile ion contamination. AZ 421K is unbuffered. AZ Developer is an alternative sodium based developer that does not etch aluminum. Developer bulletins are available with additional processing details.

Physical and Chemical Properties
The physical and chemical properties of some standard thick film products are shown in Table 1. As with all AZ products, the AZ 4000 Series photoresists are precisely manufactured and subject to stringent quality control to ensure quality and lot-to-lot consistency.

Process
1. Substrate Preparation:
Substrates should be free of organic contamination, and excessive physically adsorbed moisture. Liquid phase or vapor phase treatment with AZ Adhesion Promoter is recommended.

2. Coating:
Spray apply AZ 4901 to thickness desired or spin apply AZ 4330, 4400, or 4620. Table 2 gives nominal coating thicknesses after 90°C/30 minute postbake.

<table>
<thead>
<tr>
<th>Property</th>
<th>AZ 4330</th>
<th>AZ 4400</th>
<th>AZ 4620</th>
<th>AZ 4901</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating Method</td>
<td>Spin</td>
<td>Spin</td>
<td>Spin</td>
<td>Spray</td>
</tr>
<tr>
<td>Solids Content (%)</td>
<td>35.5 ± 1.2</td>
<td>37.2 ± 1.2</td>
<td>41.7 ± 1.4</td>
<td>21.0 ± 0.7</td>
</tr>
<tr>
<td>Kinematic Viscosity at 25°C (cSt)</td>
<td>100.0 ± 10.0</td>
<td>140.0 ± 15.0</td>
<td>360.0 ± 60.0</td>
<td>6.04 ± 0.40</td>
</tr>
<tr>
<td>Absorptivity Specification (l/g cm at 398 nm)</td>
<td>0.845 ± 0.029</td>
<td>0.888 ± 0.031</td>
<td>1.00 ± 0.04</td>
<td>0.485 ± 0.016</td>
</tr>
<tr>
<td>Specific Gravity at 25°C</td>
<td>1.050 ± 0.010</td>
<td>1.060 ± 0.010</td>
<td>1.070 ± 0.010</td>
<td>0.980 ± 0.005</td>
</tr>
<tr>
<td>Water Content</td>
<td>0.5% max</td>
<td>0.5% max</td>
<td>0.5% max</td>
<td>0.5% max</td>
</tr>
<tr>
<td>Principal Solvent</td>
<td>2-ethoxyethyl acetate</td>
<td>2-ethoxyethyl acetate</td>
<td>2-ethoxyethyl acetate</td>
<td>n-butyl acetate</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clear Amber-Red</td>
<td>Clear Amber-Red</td>
<td>Clear Amber-Red</td>
<td>Clear Amber-Red</td>
</tr>
<tr>
<td>Particle Count (per sq. in.)</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Filtration</td>
<td>0.5 μm</td>
<td>0.5 μm</td>
<td>0.5 μm</td>
<td>0.2 μm</td>
</tr>
</tbody>
</table>
For large or oddly shaped substrates, roller, dip, and meniscus coating have been used with these standard products as well as with custom blends of the AZ 4000 Series photoresist.

### Table 2

<table>
<thead>
<tr>
<th>Spin Speed (rpm)</th>
<th>AZ 4330</th>
<th>AZ 4400</th>
<th>AZ 4620</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>3.6</td>
<td>4.6</td>
<td>7.1</td>
</tr>
<tr>
<td>4000</td>
<td>3.3</td>
<td>4.0</td>
<td>6.2</td>
</tr>
<tr>
<td>5000</td>
<td>2.9</td>
<td>3.5</td>
<td>5.6</td>
</tr>
<tr>
<td>6000</td>
<td>2.7</td>
<td>3.3</td>
<td>5.1</td>
</tr>
<tr>
<td>7000</td>
<td>2.5</td>
<td>3.0</td>
<td>4.7</td>
</tr>
</tbody>
</table>

3. Softbake: 90°C for 60 minutes in a convection oven (forced air is preferable for more consistent results). Extended bake time or higher bake temperature is sometimes useful for enhanced resist integrity and adhesion during subsequent processing. Shorter bake times will result in lower exposure energy requirements but also higher unexposed resist loss (lower contrast). Hot plate baking is a very effective method of baking these thick resists due to the efficient solvent removal and minimal sensitizer degradation it provides. A temperature of 100°-130°C for 50-60 seconds usually provides optimal results.

4. Exposure: Expose as required to replicate chosen photomask line space width. The exposure energy requirement will vary according to resist thickness, developer concentration and time schedule selected. For resist films greater than 4 microns use 50 mJ/cm² per micron of resist as a starting point for exposure energy, and vary as necessary to replicate CD's.

5. Development: For optimal performance, thick films should be batch immersion developed. For resist films from 4 to 8 micrometers a two-minute immersion process in AZ 400K diluted 1:3 (one part developer to 3 parts D.I. water) or AZ 421K undiluted offers excellent speed and latitude with good contrast. For thicker films (8-12 micrometers), a three to five-minute process may be used. Developer should be maintained at a constant temperature (±1°C) within the range of 20°C-25°C. Develop waters with mgl agitation in the plane of the washers. For film thicknesses greater than 12 μm, increase the developing time as required.

6. Rinse: D.I. water until resistivity is within required limits.

7. Postbake: Postbaking will generally improve image stability and adhesion, as well as chemical and plasma etch resistance. The temperature and time of postbake will depend on the nature of the resist process and should be determined experimentally. It may be necessary to hold postbake to 1-120°C in thick films due to the higher residual solvent content. For high temperature, plasma etching and ion implantation processes, resist integrity may be improved by special stabilization techniques. The AZ 4000 Series resist is resistive to deep UV stabilization techniques which allow the photoresist to be baked at temperatures up to 200°C. Typically a 2-3J/cm² photoflood of 200-300 nm UV radiation is used at 100°C followed immediately by hard bake at over 180°C. This gives good stabilization to harsh etching or implant conditions and improved reposition resistance. A pre-cycle using the PRISIT™ process or a high temperature post-exposure (pre-development) bake is also helpful in maintaining image integrity in harsh plasma conditions.

8. Stripping: AZ 4000 Series resists which have been postbaked at temperatures below 120°C can usually be stripped with AZ Thinner or electronic grades of n-butyl acetate, acetone and similar solvents. When postbake temperatures exceeding 120°C have been used, Caro's acid, commercial stripper products or oxygen plasma stripping is recommended.

### Coating Process for Films Thicker Than 8 μm

AZ 4620 is the standard formulation with the highest solids content which gives a filmable solution. The maximum thickness that can be obtained in a conventional spin coating process is 8 μm. Thicker films with uniformity of ±5% can be obtained by controlled evaporation of solvent during the coating process. A process sequence that can be used to obtain 12 μm films is as follows:

1. Flood: center of wafer with 3-4 ml of AZ 4620.
2. Spin: at 1750 rpm for 9 seconds.
3. Instantaneously decrease spin speed to 1000 rpm for 60 seconds.
4. Instantaneously increase spin speed to 7000 rpm for 10 seconds.
5. Thinner or thicker films can be obtained by varying the spin speed of Step 3. Multiple coating is necessary to build up film thicknesses greater than 15 μm with AZ 4600. The following sequence is used to build up to 25 μm of resist on 3 inch wafers:

   1. Flood: water center and spin at 1250 rpm for 30 seconds.
   2. Oven bake at 90°C for 5 minutes.
   3. Flood: water center and spin at 1250 rpm for 30 seconds.
   4. Bake at 90°C for 30 seconds.
   5. Remove edge bead.

### Spray Coating
AZ 4901 photoresist has a more volatile solvent system specially formulated for spray application. With spray coating, ultra-thin (up to 30 μm) films of AZ 4000 photoresist can be obtained.

To optimize coating characteristics in a particular spray application, the AZ applications staff may recommend other standard or custom AZ 4000 Series photoresists. The solids content, solvent system and additives in the selected photoresist will affect the film characteristics in a given spray application, while the processing characteristics will be primarily a function only of the final coating thickness.

### Other Coating Techniques
AZ 4330 would be recommended for initial evaluation in a roller or meniscus coating operation. The photoresist recommended for a dip coating operation would depend on the substrate, the desired withdrawal rate and the desired coating thickness.

### Discussion
The exceptional properties of the AZ 4000 Series are largely a result of its absorption characteristics. The ultraviolet spectrum in Figure 1 shows that after photo-bleaching greater than 80% of the light is transmitted through a 1 μm thick film over most of the useful spectrum. In comparison, a conventional photoresist may transmit only 20-30% under similar conditions. This high transparency of the AZ 4000 Series is obtained by utilizing a superior sensitizer that is effective at unusually low concentrations. The high transparency directly relates to the ability to print in exceptionally thick planarizing films with remarkable edge acuity. Note in Figure 2 the excellent planarization, the greater than 2:1 aspect ratio and the exact line and space replication at all dimensions indicating no overexposure.

![Figure 1. AZ 4000 spectral transmission (1 μm).](image1.jpg)

The ability to generate patterns with aspect ratios greater than 2:1 allows AZ 4000 Series photoresist to maintain extremely good resolution, even in thick films. This, combined with enhanced plasma resistance, gives an outstanding photoresist for etching operations as shown in Figure 3.

![Figure 2. AZ 4330, 3.3 μm on VLSI Topography (Al/Cu surface), 50°C, 30 minute softbake, imaged with 436 nm stepper, 90°C post exposure bake, AZ Developer 1:1 dilution immersion developed.](image2.jpg)

The ability to produce excellent images in extremely thick resist films is shown in Figure 4. A 25 μm resist layer produced as described above was imaged to give the 10x14 μm, 32x40 μm and 32x75 μm features shown.

![Figure 3. AZ 4330, 3.3 μm on 5700 A polysilicon, 2 μm 1:1 exposure at 185 mJ/cm² with Perkin-Elmer 220 Micralign, developed with AZ 400K 1:4 for 2.5 min., plasma etched.](image3.jpg)
For large or oddly shaped substrates, roller, dip, and meniscus coating have been used with these standard products as well as with custom blends of the AZ 4000 Series photoresists.

**Table 2**

<table>
<thead>
<tr>
<th>Spin Speed (rpm)</th>
<th>AZ 4330</th>
<th>AZ 4400</th>
<th>AZ 4620</th>
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<td>5.1</td>
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<tr>
<td>7000</td>
<td>2.5</td>
<td>3.0</td>
<td>4.7</td>
</tr>
</tbody>
</table>

3. Softbake: 90°C for 60 minutes in a convection oven (forced air is preferable for more consistent results). Extended bake time or higher bake temperature is sometimes useful for enhanced resist integrity and adhesion during subsequent processing. Shorter bake times will result in lower exposure energy requirements but also higher unexposed resist loss (lower contrast). Hot plate baking is a very effective method of baking these thick resists due to the efficient solvent removal and minimal sensitizer degradation it provides. A temperature of 100°C-120°C for 50-60 seconds usually provides optimal results.

4. Exposure

Exposure as required to replicate chosen photomask line/space width. The exposure energy requirement will vary according to resist thickness, developer concentration and time schedule selected. For resist films greater than 4 microns use 50 mJ/cm² per microm of resist as a starting point for exposure energy, and vary as necessary to replicate CD's.

5. Development:

For optimal performance, thick films should be batch immersion developed. For resist films from 4 to 8 micrometers a two minute immersion process in AZ 400K diluted 1:3 (one part developer to 3 parts D.I. water) or AZ 421K undiluted offers excellent speed and latitude with good contrast. For thicker films (8-12 micrometers), a three to five minute process may be used. Developer should be maintained at a constant temperature (+1°C) within the range of 20°C-25°C. Develop waters with mid agitation in the plane of the wafers. For film thicknesses greater than 12 µm, increase the developing time as required.

6. Rinse:

D.I. water until resistivity is within required limits.

7. Postbake: Postbaking will generally improve image stability and adhesion, as well as chemical and plasma etch resistance. The temperature and time of postbake will depend on the nature of the resist process and should be determined experimentally. It may be necessary to hold postbake to 110°C-120°C in thick films due to the higher residual solvent content. For high temperature plasma etching and dry development processes, resist integrity may be improved by special stabilization techniques. The AZ 4000 Series resists are responsive to deep UV stabilization techniques which allow the photoresist to be baked at temperatures up to 200°C. Typically a 2-30 J/cm² photofield of 254-365 nm UV radiation is used at 100°C followed immediately by hardbake at over 180°C. This gives good stabilization to harsh etching or implant conditions and improved delamination resistance. A pre-cycle using the PRIST process or a high temperature post-exposure (pre-development) bake is also helpful in maintaining image integrity in harsh plasma conditions.

8. Stripping:

AZ 4000 Series resists which have been postbaked at temperatures below 120°C can usually be stripped with AZ Thinner or similar grades of n-butyl acetate, acetone and similar solvents. When postbake temperatures exceeding 120°C have been used, Caro's acid, commercial stripper products or oxygen plasma stripping is recommended.

Coating Process for Films Thicker Than 8 µm

AZ 4620 is the standard formulation with the highest solids content and gives a filigree solution. The maximum thickness that can be obtained in a conventional spin coating process is 8 µm. Thicker films with uniformity of ±5% can be obtained by controlled evaporation of solvent during the coating process. A process sequence that can be used to obtain 12 µm films is as follows:

1. Flood center of wafer with 3-4 ml of AZ 4620.
2. Spin at 1750 rpm for 9 seconds.
3. Instantaneously decrease spin speed to 1000 rpm for 60 seconds.
4. Instantaneously increase spin speed to 7000 rpm for 10 seconds.

Thinner or thicker films can be obtained by varying the spin speed of Step 3. Multiple coating is necessary to build up film thicknesses greater than 15 µm with AZ 4620. The following sequence is used to build up 25 µm of resist on 3 inch wafers:

1. Flood wafer center and spin at 1250 rpm for 30 seconds.
2. Oven bake at 90°C for 5 minutes.
3. Flood wafer center and spin at 1250 rpm for 30 seconds.
4. Bake at 90°C for 30 seconds.
5. Remove edge bead.

Spray Coating:

AZ 4901 photoresist has a more volatile solvent system specially formulated for spray application. With spray coating, ultra-thin (up to 500 µm) films of AZ 4000 photoresist can be obtained.

To optimize coating characteristics in a particular spray application, the AZ applications staff may recommend other standard or custom AZ 4000 Series photoresists.

The solids content, solvent system and additives in the selected photoresist will affect the film characteristics in a given spray application, while the processing characteristics will be primarily a function only of the final coating thickness.

Other Coating Techniques

AZ 4330 would be recommended for initial evaluation in a roller or meniscus coating operation. The photoresist recommended for a dip coating operation would depend on the substrate, the desired withdrawal rate and the desired coating thickness.

Discussion

The exceptional properties of the AZ 4000 Series are largely a result of its adsorption characteristics. The ultraviolet spectrum in Figure 1 shows that after photo-bleaching greater than 80% of the light is transmitted through a 1 µm thick film of most of the useful spectrum. In comparison, a conventional photoresist may transmit only 20-30% under similar conditions. This high transparency of the AZ 4000 Series is obtained by utilizing a superior sensitizer that is effective at unusually low concentrations. The high transparency directly relates to the ability to print in exceptionally thick planarizing films with remarkable edge acuity. Note in Figure 2 the excellent planarization; the greater than 2:1 aspect ratio and the exact line and space replication at all dimensions indicating no overexposure.

The ability to generate patterns with aspect ratios greater than 2.1 allows AZ 4000 Series photoresists to maintain extremely good resolution, even in thick films. This, combined with enhanced plasma resistance, gives an outstanding photoresist for etching operations as shown in Figure 3.

The ability to produce excellent images in extremely thick resist films is shown in Figure 4. A 25 µm resist layer produced as described above was imaged to give the 10x16 µm, 32x60 µm and 32x72 µm features shown.
mists. Wear chemical goggles, rubber gloves, and protective clothing. The flash points are as follows:

<table>
<thead>
<tr>
<th>Product</th>
<th>Flash Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ 4330</td>
<td>106°F</td>
</tr>
<tr>
<td>AZ 4400</td>
<td>106°F</td>
</tr>
<tr>
<td>AZ 4620</td>
<td>98°F</td>
</tr>
<tr>
<td>AZ 4901</td>
<td>95°F</td>
</tr>
<tr>
<td>AZ Thinner</td>
<td>109°F</td>
</tr>
</tbody>
</table>

First Aid

**If swallowed**, give two glasses of water. Never give anything by mouth to an unconscious person.

**If inhaled**, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen.

**In case of contact**, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes.

**Call a physician.**

Please consult Material Safety Data Sheets for further information.

Emergency Telephone Number:
(201) 231-2244 Including medical emergencies.

NOTE:
The developers for these photoresists are alkaline solutions. Handle with care. Avoid contact with skin and eyes. Avoid breathing mists. Wear chemical goggles, rubber gloves and protective clothing.

Materials Storage

Protect from light and heat. Shelf life is guaranteed for one year from date of delivery when stored at 30-70°F. Keep in sealed original containers away from oxidants, sparks, and open flames.

References

Description and Applications
AZ 4903 photoresist provides unmatched capabilities in applications requiring spin-on film thicknesses of 7-30 μm (0.3 - 1.2 mil). Typical applications include bump plating for tape automated bonding and flip chip technologies, thin film magnetic heads, displays, IR arrays, solar cells, ceramic packaging, etc. Features of AZ 4903 photoresist that make it ideal for these applications are:

- Exceptional transparency which allows a 30 μm film to be exposed with only 500-1000 mJ/cm².
- Broad spectral sensitivity - superior response to exposure sources ranging from 310-436 nm (UV3 and UV4).
- Steep wall profiles - ideal for up-plating.
- Good adhesion in alkaline or acidic plating baths.
- Suitable for contact, proximity or projection printing.

It is important to note that success with the thickest AZ 4903 films requires that special attention be paid to certain processing steps. This includes extra effort to minimize or eliminate edge bead, optimization of softbake, and careful control of hold time between softbake and exposure. The specifics are discussed in the process section of this note.

Companion Developer
AZ 421K is the recommended developer for ultra-thick AZ 4903 photoresist applications. It is an unbuffered potassium based developer that provides the process latitude associated with inorganic developers while minimizing the risk associated with mobile ion contamination. A developer bulletin is available with additional processing details.¹

Physical and Chemical Properties
The physical and chemical properties are shown in Table 1. As with all AZ products, AZ 4903 photoresist is precisely manufactured and subject to stringent quality control procedures to ensure lot-to-lot consistency.

### Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids content (%)</td>
<td>47.0 ± 1.9</td>
</tr>
<tr>
<td>Kinematic viscosity at 25°C (cSt)</td>
<td>1350 ± 230</td>
</tr>
<tr>
<td>Absorptivity specification (l/g cm at 398 nm)</td>
<td>1.10 ± 0.05</td>
</tr>
<tr>
<td>Specific gravity at 25°C</td>
<td>1.090 ± 0.010</td>
</tr>
<tr>
<td>Water content</td>
<td>0.75% max</td>
</tr>
<tr>
<td>Principle solvent</td>
<td>2-ethoxyethyl acetate</td>
</tr>
<tr>
<td>Appearance</td>
<td>Clear Amber-Red</td>
</tr>
<tr>
<td>Particle count (particles/in³, 10 μm spin coat)</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

#### Process
1. **Substrate Preparation:** Substrates should be free of organic contamination and excessive physically adsorbed moisture. Vapor phase treatment with AZ Adhesion Promoter is recommended.
2. **Spin Coating:** Approximate coating thickness after 90°C/30 minute convection oven softbake is given in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Spin Speed (rpm)</th>
<th>Thickness after 90°C Softbake (μm)</th>
<th>Thickness after 90°C Softbake (mils)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>30.0</td>
<td>1.2</td>
</tr>
<tr>
<td>1000</td>
<td>23.5</td>
<td>0.93</td>
</tr>
<tr>
<td>2000</td>
<td>14.6</td>
<td>0.57</td>
</tr>
<tr>
<td>3000</td>
<td>13.1</td>
<td>0.52</td>
</tr>
<tr>
<td>4000</td>
<td>10.7</td>
<td>0.42</td>
</tr>
<tr>
<td>5000</td>
<td>9.1</td>
<td>0.36</td>
</tr>
<tr>
<td>6000</td>
<td>8.0</td>
<td>0.31</td>
</tr>
<tr>
<td>7000</td>
<td>7.2</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Most ellipsometry and interferometry based film thickness monitors are not calibrated to read the exceptionally thick films obtained with AZ 4903
photoresist. A surface profile measuring system or dedicated ultra-thick film ellipsometer or interferometer should be used to measure resist thickness.

AZ 4903 produces a significant edge bead when spun using conventional procedures. The spin process Table 3 was developed on an SSVG coater equipped with front and backside rotate to eliminate the edge bead. The process time can be shortened if some edge bead can be tolerated.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Step</th>
<th>Operation</th>
<th>Time (sec)</th>
<th>Speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dispense - static</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Spin</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Spin</td>
<td>2000</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Spin</td>
<td>2400</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Back edge bead removal</td>
<td>5-10</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Front edge bead removal</td>
<td>3-10</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Spin</td>
<td>5</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>End</td>
<td></td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

If hot plate bake is used, both front and back edge bead removal with AZ EBR Solvent or AZ Thinner is required if complete edge bead removal is desired. If waters are convection oven baked, back edge bead removal alone may be sufficient. Some processes, such as plating, require that resist cover the entire wafer including the edge. For these processes, AZ 4110 photoresist is recommended instead of solvent or thinner for top edge bead removal because it will eliminate edge bead, yet keep the wafer edge covered with resist.

The unusually long spin time in Step 5 may limit coater throughput, but is necessary to dry the film sufficiently to prevent solvent reabsorption during edge bead removal. A 60 second hot plate bake at 85-90°C after a 20-60 second spin cycle also accomplishes similar drying, but may require special coating/hot plate equipment.

The 5 second spin at Step 6 dries the wafer after edge bead removal. A longer spin time may affect film thickness.

If a large edge bead is unacceptable on square or other non-round substrates where edge bead removal is more difficult, resist coatings up to 50 μm may be obtained by spray coating AZ 4901 or AZ 4902 photoresists, or roller, dip or mercuric coating AZ 4300 photoresist.

Softbake: AZ 4903 photoresist must be softbaked at a high enough temperature to prevent the resist from popping or cracking during exposure. This phenomenon is most likely to be caused by nitrogen, generated during exposure, channeling to the surface. A hot plate bake of 110-130°C for 90-180 seconds minimizes this effect. A 100-120°C forced air convection oven bake for 30-60 minutes also provides desirable results. These elevated softbake temperatures will increase exposure energy requirements.

4. Hold Time Between Softbake and Exposure: Ultra-thick films generally require a hold time between softbake and exposure. This is due to the need for sufficient moisture to complete the photochemical reaction during exposure. Ultra-thick films require a significantly longer time to absorb this moisture than standard thickness films. A 30 μm thick film, hot plate softbaked at 110°C, requires about 20 minutes at 30-50% relative humidity between softbake and exposure. Nitrogen scavengers do not provide such an environment, insufficient moisture absorption can result in completely developed rings around the outside of incompletely developed patterns. This is most likely due to moisture diffusing from the unexposed resist during exposure.

A long hold time between softbake and exposure (2-4 hours) can result in surface defects or "mouselle" along the top edge of a pattern. If a longer hold time is required, nitrogen desiccator storage after sufficient moisture absorption is recommended.

5. Exposure: Exposure as required to replicate a chosen photomask line/space width. The exposure energy requirements will vary according to resist thickness, baking conditions and developer time selected. Start with exposure energies of 25-50 μJ/cm² per μm of required CD. Refer to Figure 1.

6. Development: The recommended developer is AZ 421K concentrate. It is suitable for both batch immersion and in-line developing. Temperature should be maintained at 4°C within the range of 20-25°C.

Batch Immersion Development: AZ 421K concentrate, in a 1:3 rinse immersion process, offers excellent latitude and speed along with good contrast. Mild agitation of the wafer or circulation of the developer along the wafer plane is recommended for uniform development. Developer life is dependent on the amount of carbonyl dioxide absorbed from the air and by the amount of photoreist dissolved. Developer should be replenished at least once a week or when the activity is observed to be reduced.

In-line development - spray only: A typical spray in-line process with AZ 421K concentrate is:

a. Wet wafer in a water spray for 0-5 sec at 100-3000rpm
b. Spray develop for 60-90 sec at 100-3000rpm
c. Overlap rinse and developer sprays for 0-5 sec at 100-3000rpm
d. Rinse for 10-15 sec at 100-3000rpm
e. Spin dry for 5-15 sec at 4000-5000rpm

Metal-ion-free development: If a metal-ion free developer is required, AZ 440 MIF concentrated or AZ 312 MIF, mixed parts developer to 3 parts water, can be used in either batch immersion or in-line development.

7. Rinse: Rinse with DI water until resistivity is within required limits.

8. Postbake: Postbaking will generally improve image stability and adhesion during etching and plating. The extent of postbaking, if required, will depend on the nature of the entire process and should be determined by the user. Due to higher solvent content of thick films after softbake, thermal flow tends to occur at lower temperatures than with thin films of similar photoresists. It is recommended that the postbake temperature not exceed the softbake temperature by more than 5-10°C to avoid rounding of the resist images. Postbake and postbake cycles longer than the typical 30 minutes in a convection oven or 45-90 seconds on a hot plate will help maintain the resist integrity during subsequent processing.

9. Stripping: AZ 4903 photoresist which has been baked below 120°C can usually be stripped with AZ Thinner, AZ EBR solvent, or electronic grades of n-butyl acetate, acetone and similar solvents. When bake temperatures exceeding 120°C have been used, AZ 3007 photoresist stripper or oxygen plasma stripping are recommended.

Discussion

The exceptional imaging characteristics of AZ 4000 series photoresists, including AZ 4903, result directly from their absorption characteristics. The ultraviolet spectrum in Figure 1 shows that after photobleaching, more than 60% of the light is transmitted through a 1 μm thick film over most of the useful spectrum. In comparison, a conventional photoresist may transmit only 20-30% under similar conditions. This high transparency is obtained by utilizing a special sensitizer that is effective at unusually low concentrations and results in the ability to print in thick films with superior edge acuity.

![Figure 1. AZ 4000 series spectral transmission (1 μm).](image)

The ability to generate patterns with at least a 3:1 aspect ratio and high contrast is shown in Figures 2, 3, & 4. This resolution and contrast makes AZ 4903 an ideal photoreist for bump plating for IAB and flip chip technologies.
photore sist. A surface profile measuring system or dedicated ultra-thick film ellipsometer or interferometer should be used to measure resist thickness.

AZ 4903 produces a significant edge bead when spun using conventional procedures. The spin process in Table 3 was developed on an SVG coater equipped with front and backside rates to eliminate the edge bead. The process time can be shortened if some edge bead can be tolerated.

### Table 3

<table>
<thead>
<tr>
<th>Step</th>
<th>Operation</th>
<th>Time</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dispense - static</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Heat</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Spin</td>
<td>2000</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Spin</td>
<td>2400</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Edge bead removal</td>
<td>5-10</td>
<td>700</td>
</tr>
<tr>
<td>6</td>
<td>Edge bead removal</td>
<td>3-10</td>
<td>700</td>
</tr>
<tr>
<td>7</td>
<td>Spin</td>
<td>5000</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>End</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

If hot plate bake is used, both front and back edge bead removal with AZ EBR Solvent or AZ Thinner is required if complete edge bead removal is desired. If Waters are convection oven baked, back edge bead removal alone may be sufficient. Some processes, such as plating, require that resist cover the entire wafer including the edge. For these processes, AZ 4110 photore sist is recommended instead of solvent or thinner for top edge bead removal since it will eliminate edge bead, yet keep the wafer edge covered with resist.

The unusually long spin time in Step 5 may limit coater throughput, but is necessary to dry the film sufficiently to prevent solvent reabsorption during edge bead removal. A 60 second hot plate bake at 85-90°C after a 20-60 second spin cycle also accomplishes similar drying, but may require special coating/hot plate equipment.

The 5 second spin at Step 8 dries the wafer after edge bead removal. A longer spin time may affect film thickness.

If a large edge bead is unacceptable on square or other non-round substrates where edge bead removal is more difficult, resist coatings up to 50 μm may be obtained by spray coating AZ 4901 or AZ 4902 photore sist, or roller, dip or meniscus coating AZ 4300 photore sist.

3. Softbake: AZ 4903 photoresist must be softbaked at a high enough temperature to prevent the resist from popping or cracking during exposure. This phenomenon is most likely to be caused by moisture, generated during exposure, channeling to the surface. A hot plate bake of 110-130°C for 90-180 seconds minimizes this effect. A 100-120°C forced air convection oven bake for 30-60 minutes also provides desirable results. These elevated softbake temperatures will increase exposure energy requirements.

4. Hard Bake Between Softbake and Exposure: Ultra-thick films generally require a hold time between softbake and exposure. This is to give the resist sufficient moisture to complete the photochemical reaction during exposure. Ultra-thick films require a significantly longer time to absorb this moisture than standard thickness films. A 30 μm thick film, hot plate softbaked at 110°C, requires about 20 minutes at 30-50% relative humidity between softbake and exposure. Nitrogen dessicants do not provide such an environment. Insufficient moisture absorption can result in completely developed rings around the outside of incompletely developed patterns. This is most likely due to moisture diffusing from the unexposed resist during exposure.

A long hold time between softbake and exposure (2-4 hours) can result in surface defects or "mous-blies" along the top edge of a pattern. If a longer hold time is required, nitrogen dessicant storage after sufficient moisture absorption is recommended.

5. Exposure: Exposure as required to replicate a chosen photomask line/space width. The exposure energy requirement will vary according to resist thickness, baking conditions and developer time selected. Start with exposure energies of 25-50 mJ/cm² per μm of required line/space width.

6. Development: The recommended developer is AZ 421K concentrate. It is suitable for both batch immersion and in-line developing. Temperature should be maintained at 1°C within the range of 20-25°C.

Batch Immersion Development: AZ 421K concentrate, in a 1:3 minute immersion process, offers excellent latitude and speed along with good contrast. Mild agitation of the wafer or circulation of the developer along the wafer plane is recommended for uniform developing. Developer bath life is dependent on the amount of carbon dioxide absorbed from the air and by the amount of photore sist dissolved. Developer should be replenished at least once a hour or when activity is found to be reduced.

In-line development - spray only: A typical spray in-line process with AZ 421K concentrate is:

- Wet wafer in a water spray for 0-5 sec at 100-300ppm
- Spray developer for 60-90 sec at 100-300ppm
- Overlap rinse and developer sprays for 0-5 sec at 100-300ppm
- Rinse for 10-15 sec at 100-300ppm
- Spin dry for 5-15 sec at 4000-5000rpm

Metal-ion-free development: If a metal-ion-free developer is required, AZ 440 MIF concentrated or AZ 321 MF, mixed parts developer to 3 parts water, can be used in either batch immersion or in-line development.

7. Rinse: Rinse with DI water until resistivity is within required limits.

8. Postbake: Postbaking will generally improve image stability and adhesion during etching and plating. The extent of postbaking, if required, will depend on the nature of the entire process and should be determined by the user.

Due to the higher solvent content of thick films after softbake, thermal flow tends to occur at lower temperatures than with thin films of similar photoresists. It is recommended that the postbake temperature not exceed the softbake temperature by more than 5-10°C to avoid rounding of the resist images. Softbake and postbake cycles longer than the typical 30 minutes in a conventional oven or 45-60 seconds on a hot plate will help maintain the resist integrity during subsequent processing.

9. Stripping: AZ 4903 photoresist which has been baked below 120°C can usually be stripped with AZ Thinner, AZ EBR solvent, or electronic grades of n-butyl acetate, acetone and similar solvents. When bake temperatures exceeding 120°C have been used, AZ 3007 Photore sist Stripper or oxygen plasma stripping are recommended.

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**Discussion**

The exceptional imaging characteristics of AZ 4000 series photoresists, including AZ 4903, result directly from their absorption characteristics. The ultraviolet spectrum in Figure 1 shows that after photobleaching, more than 60% of the light is transmitted through a 1 μm thick film over most of the useful spectrum. In comparison, a conventional photore sist may transmit only 20-30% under similar conditions. This high transparency is obtained by utilizing a special sensitizer that is effective at unusually low concentrations and results in the ability to print in thick films with superior edge acuity.

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**Figure 1. AZ 4000 series spectral transmission (1 μm).**

The ability to generate patterns with at least a 3:1 aspect ratio and high contrast is shown in Figures 2, 3, & 4. This resolution and contrast makes AZ 4903 an excellent photoresist for bump plating for IAS and flip chip technologies.
Recommended Process Development Sequence
The suggested sequence for developing a process with AZ 4903 is as follows:

- Starting with the recommended spin cycle, adjust spin speeds and times to obtain the desired film thickness and edge bead.
- Start with:
  - 110°C softbake for 180 seconds on a hot plate or 60 minutes in a convection oven.
  - Use 45 minute to 2 hour hold time between softbake and exposure. This interval should ensure complete development under a wide variety of environmental conditions and can be widened after process optimization.
  - Develop with a 90 second in-line spray or 2 minute immersion process.
- Adjust exposure energy until patterns are clear.
- Optimize process by adjusting softbake time and temperature, development time, and exposure to replicate CD’s and achieve desired profile, process latitude and throughput.
- After process optimization, the hold time between softbake and exposure should be expanded to allow more production flexibility. Using the optimized process, vary the hold time between softbake and exposure from 0 min - 8 hours in 5 minute increments at short times (0-30 min.), in 10 minute increments at medium times (30-60 min.), and in 30 minute increments at long times (>60 min.). Inspect for pattern clearing and “mousebites.”
- To further expand the hold time latitude, repeat the previous experiment to determine hold time with wafers stored in a nitrogen dessicator after sufficient moisture absorption.

Equipment Compatibility
The AZ 4000 Series photoresists are compatible with most commercially available wafer and photomask processing equipment. Recommended materials of construction include stainless steel, glass, ceramic, PTFE, polypropylene, and high density polyethylene.

General Environmental Conditions
Process consistency of positive resists can be affected by fluctuating environmental conditions. Ambient conditions should be maintained at constant levels within the ranges of 65-80°F and 30-50% RH. Photoresists and developers stored in a cold room should be ther-}

mally equilibrated to operating temperature before use. AZ 4000 Series resists and coated substrates should be handled under yellow safelight.

Handling Precautions and First Aid
AZ 4903 is a D.O.T. combustible liquid (flashpoint 110°F). Handle it with care, keeping away from heat, sparks and flames. Use adequate ventilation. This product may be harmful if swallowed, inhaled or on contact. Avoid contact with liquid, vapors or spray mists. Wear chemical goggles, rubber gloves, and protective clothing.

FIRST AID: Take action as follows:

If swallowed, give two glasses of water. Never give anything by mouth to an unconscious person.

If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen.

In case of contact, immediately flush eyes or skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes.

Call a physician.

NOTE: The developer for this photoresist is an alkaline solution. Handle with care. Avoid contact with skin and eyes. Avoid breathing mists. Wear chemical goggles, rubber gloves and protective clothing.

EMERGENCY PHONE NUMBER: (201) 231-2244 including medical emergencies.

Please consult Material Safety Data Sheets for further information.

MATERIALS STORAGE
Protect from light and heat. Shelf life is guaranteed for six months from date of delivery when stored at 30-70°F. Keep in sealed original containers away from oxidants, sparks and open flames.

FOR INDUSTRIAL USE ONLY.

References
1 See AZ Bulletin “AZ Photore sist Developers - Inorganic.”
2 See AZ Bulletin “AZ 4000 Series Photore sist s for Thick Film Applications.”

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