AZ® 1500 SERIES POSITIVE PHOTORESISTS

Description

The AZ 1500 Series photoresists were developed in response to a growing industry desire for a positive resist containing no 2-ethoxyethyl acetate (EGEEA, EEA, CA, etc.). The AZ 1500 Series photoresists have the same photosensitizer and resin constituents as our AZ 1300 Series resists[1] but are formulated in a new solvent. This new solvent has been carefully chosen and formulated into a product[2] which emulates and can be substituted directly for the AZ 1300 Series resists with minimal process modification. Extensive testing has shown that the AZ 1500 Series resists will offer the user no compromises and many advantages. Standard dyed AZ 1500-SFD photoresists comparable to the AZ 1300-SFD products minimize reflective notching and provide optimum linewidth control[3].

Notable AZ 1500 Series features include:

- Contains no 2-ethoxyethyl acetate or xylene.
- Identical photosensitizer and resin as the well established AZ 1300 Series products.
- Comparable coating thickness and functional properties to the corresponding AZ 1300 Series products.
- Striation-free coatings.
- Lower unexposed resist loss compared to AZ 1300 Series products, see Table 3.
- Superior lot-to-lot consistency and quality.

Some applications for which the AZ 1500 Series materials are recommended include:

- Step-and-repeat, scanning projection, contact and proximity printing applications using 365, 405, and 436 nm radiation.
- Resist thicknesses ranging from 1.0-2.0 μm.
- In-line or batch development using metal-ion-free, sodium or potassium based developers.
- Wet or dry etching of oxides, nitrides, polysilicon and metals.
- Mask making.

A full range of developers are available for the AZ 1500 Series resists.

AZ 312 MIF—Metal-ion-free developer providing high throughput and process control in applications where the risk of mobile ion contamination must be eliminated.

AZ 327 MIF—Metal-ion-free developer, with optimized wetting characteristics for in-line and immersion processing to produce exceptionally clean patterns.

AZ Developer—Sodium based developer which provides optimal process control while minimizing the attack of aluminum surfaces.

AZ 351—Sodium based, buffered developer designed for optimal process control.

AZ 400K—Potassium based, buffered developer which provides optimal process control while minimizing contamination risks through use of the less mobile potassium ion.

These developers are available in high sensitivity and high contrast formulations. Developer bulletins should be requested for additional processing details.

The AZ 1500 Series resists are available in two standard viscosities to accomodate various processes and film thickness requirements:

Product	AZ 1300 Series Equivalent	Coating Thickness Range
AZ 1512	AZ 1370-SF	1.0 - 1.4 μm
AZ 1512-SFD	AZ 1312-SFD	1.0 - 1.4 μm
AZ 1518	AZ 1350J-SF	1.4 - 2.1 μm
AZ 1518-SFD	AZ 1318-SFD	1.4 - 2.1 μm

Physical and Chemical Properties:

Physical and chemical properties are shown in Table 1. As with all AZ products, the AZ 1500 Series photoresists are precisely manufactured and subject to stringent quality control to ensure excellent quality and lot-to-lot consistency.

Table 1

Property	AZ 1512	AZ 1512-SFD	AZ 1518	AZ 1518-SFD
Solids Content	26.0±0.9	26.2±0.9	29.9±1.0	30.1±1.0
Kinematic Viscosity (cSt at 25°C)	18.7±1.0	18.8±1.0	34.2±1.5	34.5±1.5
Absorptivity (l/g cm at 398 nm)	1.13±0.09	1.25±0.08	1.30±0.10	1.42±0.10
Specific Gravity at 25°C	1.040±0.010	1.040±0.010	1.055±0.010	1.055±0.010
Water Content	0.75% max.			
Principal Solvent	propylene glycol monomethyl ether acetate			
Appearance	Clear, Amber-Red			
Coating Characteristics	Striation-free			
Particle Count (Particles per in.²)	<5			
Filterability Constant	0.010 max.			
Filtration	0.2 μm abs.			

Processing:

Process as you would the comparable AZ 1300 Series resist. A recommended process sequence is:

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. Spin-Coating—Thickness (μm) after 90°C/30 minute softbake.

Product	3000 rpm	4000 rpm	5000 rpm	6000 rpm	7000 rpm
AZ 1512	1.42	1.22	1.09	0.99	0.91
AZ 1512-SFD	1.44	1.24	1.09	1.01	0.93
AZ 1518	2.05	1.76	1.57	1.43	1.32
AZ 1518-SFD	2.05	1.78	1.60	1.46	1.35

3. Softbake — 90 ± 2°C for 30 minutes in a convection oven (forced air is preferable for more consistent results). On a hot plate 100°C for 45 seconds should produce optimal results. For optimum control of standing waves and reflective notching with AZ 1500-SFD photoresists, a softbake 40°C below a post exposure bake (PEB) is recommended. A typical PEB in a convection oven process would utilize a 50°C softbake followed by exposure and a 90°C PEB. Optimum time/temperature parameters will change somewhat with changes in film thickness and process requirements.

4. Exposure — Exposure energy requirements will vary with coating thickness, baking conditions, substrate reflectivity, and the developer concentration/time schedule. Exposure energy from 70-120 mJ/cm^2 (higher for dyed resists) is recommended as a starting point to determine energy required to replicate chosen mask linewidth.

5. Development — The high contrast and high sensitivity formulations of the developers are suitable for a 60-120 second batch immersion development. Mild agitation of the wafers or pumping of the developer should be used to ensure uniform development. High sensitivity dilutions and/or longer development times are recommended for dyed photoresists[3].

For batch and in-line developing processes, developer temperature should be maintained at a constant temperature (± 1°C) within the range of 20-25°C.

Recommended Dilutions (developer: DI water)

Developer	High Sensitivity	High Contrast
AZ 312 MIF	1:1	1:1.2
AZ 327 MIF	Prediluted	
AZ 351	1:3.5	1.5
AZ 400K	1:3	1:4
AZ Developer	2:1	1:1

In-line development applications require short development times so the high sensitivity developer formulations are recommended. A wide variety of spray, stream, and puddle combinations can be used. Typical processes are:

Spray/Puddle:

a. Wet wafer in water spray	0-5 sec	100-200 rpm
b. Spray developer	5-15 sec	100-200 rpm
c. Stop wafer and continue spray to set up puddle	0-2 sec	0 rpm
d. Puddle develop	10-30 sec	0 rpm
e. Stream on rinse	5-10 sec	100 rpm
f. Spin dry	5-10 sec	4000 rpm

Spray only:

a. Wet wafer in water spray	0-5 sec	100-200 rpm
b. Spray developer	30-40 sec	100-200 rpm
c. Overlap rinse and developer sprays	0-5 sec	100-200 rpm
d. Stream on rinse	5-10 sec	100-200 rpm
e. Spin dry	5-10 sec	4000 rpm

6. Rinse — Rinse with DI water until resistivity is within required limits.

7. Postbake — Postbaking will generally improve image stability, adhesion, and plasma and chemical resistance. The extent of postbaking, if required, will depend on the entire process and should be determined by the user.

A postbake cycle of 30 min. at 120°C is recommended for wet etching and plasma processes. Wet chemical etching in hot acids, (eg. Al, Si_3N_4 etches) may require higher bake temperatures. For high temperature plasma etching and ion implantation processes, resist integrity may be improved by special stabilization techniques. The AZ 1500 resists are responsive to deep UV stabilization techniques[4] which allow the photoresist to be baked at temperatures up to 200°C. Typically a 2-30 J/cm^2 photoflood of 200-300 nm UV radiation is used at 100°C followed by immediate hardbake at over 180°C. This gives good stabilization to harsh etching or implant conditions and improved reticulation resistance. A pre-cycle using the PRIST[5] process or a high temperature post-exposure (pre-development) bake[6] is also helpful in maintaining image integrity in harsh plasma conditions.

8. Strip — AZ 1500 resists that have been postbaked at temperatures below 120°C can usually be stripped with AZ 1500 Thinner, AZ EBR Solvent, or electronic grades of n-butyl acetate, acetone or similar solvents. When postbake temperatures exceeding 120°C have been used, Caro's acid, commercial stripper products or oxygen plasma stripping are recommended.

Discussion

There has been growing concern within the semiconductor industry about the health and safety characteristics of 2-ethoxyethyl acetate otherwise known as EGEEA or "Cellosolve® Acetate", the solvent used in the majority of optical positive photoresists, (Figure 1). In an effort to meet those concerns, AZ Photoresist Products has developed a photoresist system that does not contain any EGEEA or xylene. The AZ 1500 Series photoresists contain the same resins and sensitizers as AZ 1300 Series photoresists, formulated with propylene glycol monomethyl ether acetate (PGMEA) solvent (Figure 1).[2]

When changing to a new solvent system there are two concerns; first, what are the health and safety characteristics, and second, what are the effects on lithographic performance?

1. Health and Safety

The health and safety characteristics of the glycol ethers and glycol ether acetates have been reviewed by a Senior Toxicologist at Hoechst-Roussel Pharmaceuticals, a sister group within American Hoechst. A report based on this review is available on request to any authorized health and safety official. The conclusion of the report pertaining to PGMEA is summarized:

"Considering that the toxicological evaluation of the glycol ethers is still in proress, there appears to be a definite trend in the overall pattern of toxicity which favors the relative safety of propylene glycol ethers compared to ethylene glycol ethers."

$$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

Ethylene glycol monoethyl ether acetate — EGEEA — 2-ethoxyethyl acetate

$$CH_3\text{-}O\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}H\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

Propylene glycol monomethyl ether acetate — PGMEA — 1-methoxy-2-propyl acetate

Figure 1
Chemical structures of the solvents

It is clear from Figure 1 that EGEEA and PGMEA are similar in chemical structure. Yet it appears that these differences in chemical structure can have a significant effect on the toxicological properties of EGEEA and PGMEA. In the report it is shown that the different toxicological properties are probably a result of differences in the way the materials are metabolized.

Lithographic Performance

The key attributes of the AZ 1300 Series materials are discussed in detail in the AZ 1300 product bulletin. In this section, the lithographic performance of AZ 1500 Series materials will be compared to AZ 1300 Series materials in a high sensitivity metal-ion-free developer (AZ 312 MIF (1:1)) and a high contrast inorganic developer (AZ 351 (1:5)). The following parameters were evaluated:

Coating Characteristics
Photospeed
Contrast
Unexposed Resist Loss
Wall Angle
Rate of Change of Linewidth with Exposure Dose
Thermal Stability
Adhesion

Experimental

The AZ 1500 and AZ 1300-SF materials were processed under identical conditions. The materials were coated on an MTI coating unit so that all samples had a coating thickness of 1.4 μm. The wafers were prebaked at 90°C. for 30 minutes in a recirculating convection oven. They were exposed on a Perkin-Elmer 220 Projection Aligner operating with a slit of 1.7 mm at aperture #2.

The resists were exposed at identical scan speeds in all the examples shown. The wafers were developed for 60 seconds at 20°C using mild agitation.

Coating Characteristics

The 1500 Series contains a "striation-free" ingredient to ensure uniform coatings. The variation in film thickness across the wafers was less than 100Å with no evidence of striations when viewed under monochromatic illumination.

Photospeed, Contrast and Unexposed Resist Loss

The photospeed of a resist is easily evaluated from a plot of the fraction of photoresist remaining in the exposed regions *versus* the logarithm of exposure energy. Figure 2 shows such a plot for AZ 1518 and AZ 1350J-SF. The photospeed is given by the dose at zero resist remaining, the contrast by the slope of the line or portion of the curve near the dose-to-clear. The curves for AZ 1518 and AZ 1350J-SF are virtually indistinguishable. The standard AZ 1500 Series photoresists were specifically formulated to have photospeed values comparable to those of the equivalent AZ 1300 Series products.

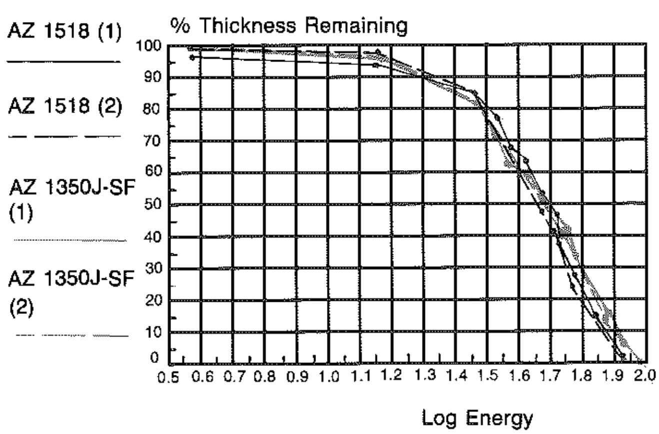


Figure 2

AZ 1350J-SF vs AZ 1518 developed with AZ 351 (1:5), 60 sec.

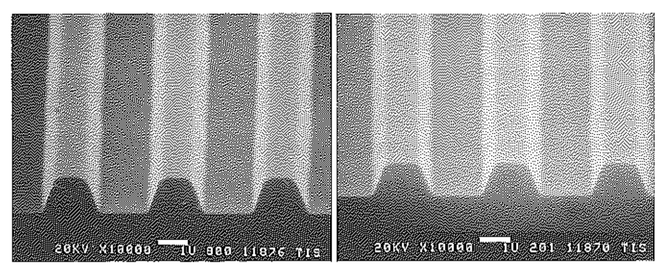
The measured values of photospeed, contrast, and unexposed resist loss are summarized in Table 3. The photospeed data, in both metal-ion-free and inorganic developers, shows a maximum difference between AZ 1500 and AZ 1300 Series of 5.9%.

Table 3

Developer	Photoresist	Photospeed (mJ/cm²)	Contrast	Unexposed Loss (A)
AZ 351 (1:5)	AZ 1512	58.0	2.3	90
	AZ 1370-SF	58.0	2.2	140
AZ 312 MIF (1:1)	AZ 1512	36.9	1.8	462
	AZ 1370-SF	36.3	1.8	845
AZ 351 (1:5)	AZ 1518	81.0	2.1	75
	AZ 1350J-SF	86.1	2.0	355
AZ 312 MIF (1:1)	AZ 1518	55.7	1.8	372
	AZ 1350J-SF	58.3	1.6	885

Wall Angle

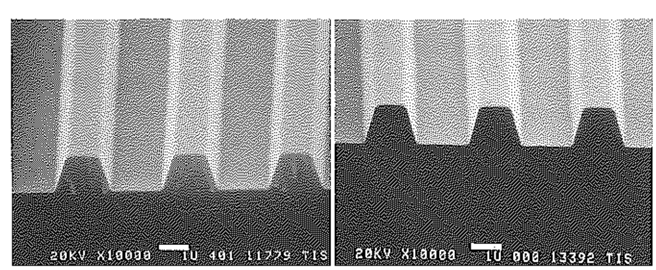
Figures 3 and 4 show 2 μm lines and spaces printed in both AZ 1512 and AZ 1518 versus the equivalent AZ 1300-SF resists. The patterns were exposed at the same scan speed, etc. and are virtually indistinguishable in linewidth, wall profile, and overall cleanliness. The slight differences are typical of lot-to-lot manufacturing tolerance.



a b

Figure 3

AZ 1370 SF (a) and AZ 1512 (b), 1.2 μm on SiO_2, 2μm l/s, developed with AZ 351 1:5, 60 sec.
Images printed on a Perkin Elmer Model 220 Projection Aligner.



a b

Figure 4

AZ 1350J-SF (a) and AZ 1518 (b), 1.5 μm on SiO_2, 2μm, l/s, developed with AZ 351 1:5, 60 sec.
Images printed on a Perkin Elmer Model 220 Projection Aligner.

Linewidth Control

The variation of linewidth and wall angle with exposure dose are shown in Figure 5; again the curves are very similar.

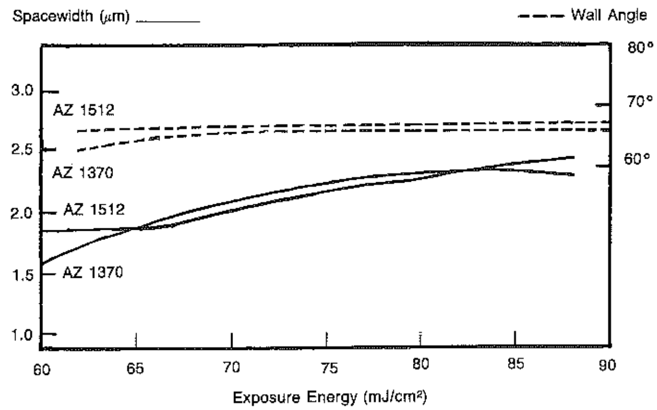


Figure 5

Process latitude (10% dose change) in AZ 312 MIF (1:1). AZ 1512 ± 0.21 μm, AZ 1370 ± 0.26 μm.
Images printed on a Perkin Elmer Model 220 Projection Printer.

Thermal Stability, Adhesion, Plasma Etch Resistance

There is extensive experimental data on all of these parameters, all of which finds no significant difference between the AZ 1500 and AZ 1300-SF series. However, experimental evidence indicates that process modification would typically be required when substituting an AZ 1500 Series for a comparable AZ 1300 Series product for lift off processes involving chlorobenzene soaks.

Summary

The AZ 1500 Series products are designed to meet the industry's need for a resist that does not contain any EGEEA. AZ 1500 is designed to be a direct replacement for AZ 1300, AZ 1300-SF and all other products based on 1300 series raw materials manufactured by AZ Photoresist Products.

Equipment Compatibility:

AZ 1500 Series photoresists are compatible with most commercially available wafer and photomask processing equipment. Recommended compatible materials include stainless steel, glass, ceramic, PTFE, high density polyethylene and polypropylene.

General Environmental Conditions

Process consistency of positive resists can be affected by fluctuating environmental conditions. Ambient temperature and humidity should be maintained at constant levels in the ranges of 65-80°F and 30-50% RH respectively. Photoresists and developers which have been stored in a cold room should be thermally equilibrated to operating temperature before use. AZ 1500 Series resists and coated substrates should be handled under yellow safelight.

Handling Precautions and First Aid:

The AZ 1500 Series photoresists are D.O.T. combustible liquids. Handle with care. Keep away from heat, sparks, and flames. Use adequate ventilation. May be harmful if swallowed, inhaled or on contact. Avoid contact with liquid, vapor or spray mist. Wear chemical goggles, rubber gloves, and protective clothing. The flash points are as follows:

Product	Flash Point
AZ 1512	116°F
AZ 1512-SFD	116°F
AZ 1518	119°F
AZ 1518-SFD	119°F

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.

Please consult Material Safety Data Sheets for further information.

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.

EMERGENCY TELEPHONE NUMBER: (201) 231-2244 Including medical emergencies.

MATERIAL 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.

FOR INDUSTRIAL USE ONLY.

References

[1]See AZ Product Bulletin "AZ 1300 Series Positive Photoresists".
[2]Protected by U.S. Patent #4,550,069. Other U.S. and foreign patents pending.
[3]See AZ Bulletins "Dyed Positive Photoresists", "Post Exposure Bake", and "AZ 1312-SFD and AZ 1318-SFD Dyed Positive Photoresists".
[4]R. Allen, M. Foster, Y. T. Yen, **J. Electrochemical Society,** Vol. 129, p. 1380 (1982). See also AZ Bulletin "Deep U.V. Curing of Positive Photoresists".
[5]W. H. L. Ma, **Proc. S.P.I.E.,** "Submicron Lithography, Vol. 333, p. 12-23 (1982).
[6]M. A. Spak, **Proc. S.P.I.E.,** "Advances in Resist Technology II", p. 299 (1985).

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