# Development of 193-nm wet BARCs for implant applications

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## ABSTRACT

This paper describes the chemistry and performance of a new family of wet-developable (wet) bottom anti-reflective coatings (BARCs) that have been developed for 193-nm implant layer applications. These BARCs, which are light sensitive and positive working, are imaged and developed in the same steps as the covering 193-nm photoresist. The BARCs are spin coated from organic solvents and then insolubilized during a hot plate bake step. The resulting cured films exhibit minimal solubility in numerous organic solvents. Resolution of a photoresist A and light-sensitive BARC I at optimum exposure (Eop) on a silicon substrate was 150-nm L/S (1:1), with good sidewall angle and no scumming. These best-case results utilize a first reflectivity minimum BARC thickness and meet the desired resolution goals for noncritical implant layers. BARC optical parameters can easily be adjusted by altering the polymeric binder. PROLITH™ modeling shows that near zero reflectance can be achieved on a silicon substrate for both a first and a second reflectivity minimum BARC thickness. The light-sensitive, wet BARCs are both spin-bowl and solution compatible with most industry standard solvents. A selected BARC from this family of wet products was shown to be stable, providing reproducible film properties over several months of ambient storage conditions.

Keywords: anti-reflective, BARC, wet-developable, implant, 193-nm microlithography

## 1. INTRODUCTION

Feature sizes will continue to shrink as device manufacturers strive to pack ever more information onto a die. Good critical dimension (CD) control will be important, even for implant processes whose dimensions are often larger than for isolation/gate/contact layers.[1] In order to keep pace, the microchip industry will soon need a 193-nm anti-reflective technique/photoresist combination for 45-nm node implants. The targeted resolution for noncritical implant layer applications is about 150-nm L/S (1:1). Potential anti-reflective procedures include a dyed resist, dyed resist plus top anti-reflective coating (TARC), and a bottom anti-reflective coating (BARC).[2,3] A dyed resist provides only limited CD control, and a TARC has no effect on reflective notching.[2] A BARC serves to improve focus/exposure latitude, reduce reflective notching and CD variations over topography, eliminate standing waves, and protect the 193-nm resist against substrate poisoning.[1] Among the three techniques, organic wet BARCs give the best CD swing control and resist sidewalls.[3] Using a wet BARC rather than a plasma-developed (dry) BARC eliminates a plasma etching step that could damage the implant area, and the former product is more cost-effective than the dry BARC that requires the extra processing step. Another disadvantage of dry BARCs is increased defectivity.[1]

The common isotropically developing wet BARCs, which typically use polyamic acids as binder polymers, usually provide lower resolution than dry BARCs.[2] Also, for polyamic acid products, the bake window in which the wet BARC is insoluble in photoresist solvents but soluble in developer is often narrow (≤10°C).[4] In the quest for a wider bake window and much improved resolution and line profiles, light-sensitive wet BARCs are being developed. As will be shown, the bake window for these new products is indeed often wider than for isotropically developing systems.

The photoresist and underlying light-sensitive BARC are exposed at the same time with 193-nm light, and both layers are subsequently processed and removed with aqueous tetramethylammonium hydroxide (TMAH) developer in the same steps. These new BARCs offer the potential for anisotropic development. Optimization of the BARCs is ongoing, with the positive-working materials expected to provide less undercutting and line collapse problems than products exhibiting isotropic development. This paper describes some of the requirements for 193-nm wet BARCs for 45-nm node implant applications. The discussions also include BARC chemistry, processing properties, optical parameters, PROLITH

modeling studies, compatibilities, product stability at room temperature, and examples of lithography versus BARC bake temperatures and at different foci.

## 2. METHODOLOGY

The safe solvents used for all described BARCs were propylene glycol monomethyl ether (PGME) and propylene glycol monomethyl ether acetate (PGMEA). The spin-coating and bake parameters varied, with contact mode used on the hot plates. A Gaertner ellipsometer was used to measure film thickness of the baked coatings on a silicon substrate. Absorbance of the cured coatings at 193 nm was measured on a quartz substrate using a Cary 500 Scan UV-Vis-NIR spectrophotometer. Optical densities (ODs) at 193 nm were then calculated from the absorbance (quartz) and thickness (silicon) data. The standard ethyl lactate (EL) stripping test (20-second puddle, spin dry at 3000 rpm for 30 seconds) was used to quantify insolubility of the baked coatings, with a product goal being no intermixing with photoresist.[5] Spin-bowl and solution compatibility testing was conducted as described in earlier publications.[6,7] The BARC's optical parameters were measured using a VUV-VASE from J.A. Woollam. The 193-nm exposures were carried out at IMEC and ASML's demo lab. Cross-sectioned wafers and the corresponding scanning electron microscope (SEM) photos were prepared at Brewer Science using, for the latter, a LEO 1560 from LEO Electron Microscopy.

## 3. RESULTS AND DISCUSSION

### 3.1 Design requirements

The following discussions will address progress in meeting most of the selected performance requirements for 193-nm wet BARCs for implant applications, which are:

a) 150-nm resolution
b) Resist profiles comparable to those given by dry-etch BARCs
   - straight sidewalls
   - clean spaces
   - minimal undercut
c) Depth of focus (DOF) of 0.3 µm or greater
d) BARC processing window ≥ 10°C
e) Spin-bowl compatible
f) Room temperature stability for 6 months
g) Development time (with resist) of 60 seconds or less with 0.26N TMAH
h) Safe solvent system

### 3.2 BARC chemistry

The experimental formulations all contain at least a dye-attached polymer, crosslinkers, photoacid generators (PAGs), quenchers, and solvents. The BARC films are solvent-soluble prior to a hot plate bake. During the hot plate bake, the solvent is removed, and pendant acidic functional groups (A) on the polymer react with functional groups B on the crosslinker to produce a solvent-insoluble product. The crosslinked product does not intermix with the photoresist during the latter's application and post-application bake (PAB). As a result of a 193-nm light-exposure step and subsequent post-exposure bake (PEB), the acidic functional group A on the polymer is regenerated, providing for developer solubility in the light-exposed areas. Decomposition by-products C and D are formed from the crosslinker during the deprotection step and are removed during the development and rinse steps. This chemistry is depicted in Figure 1.

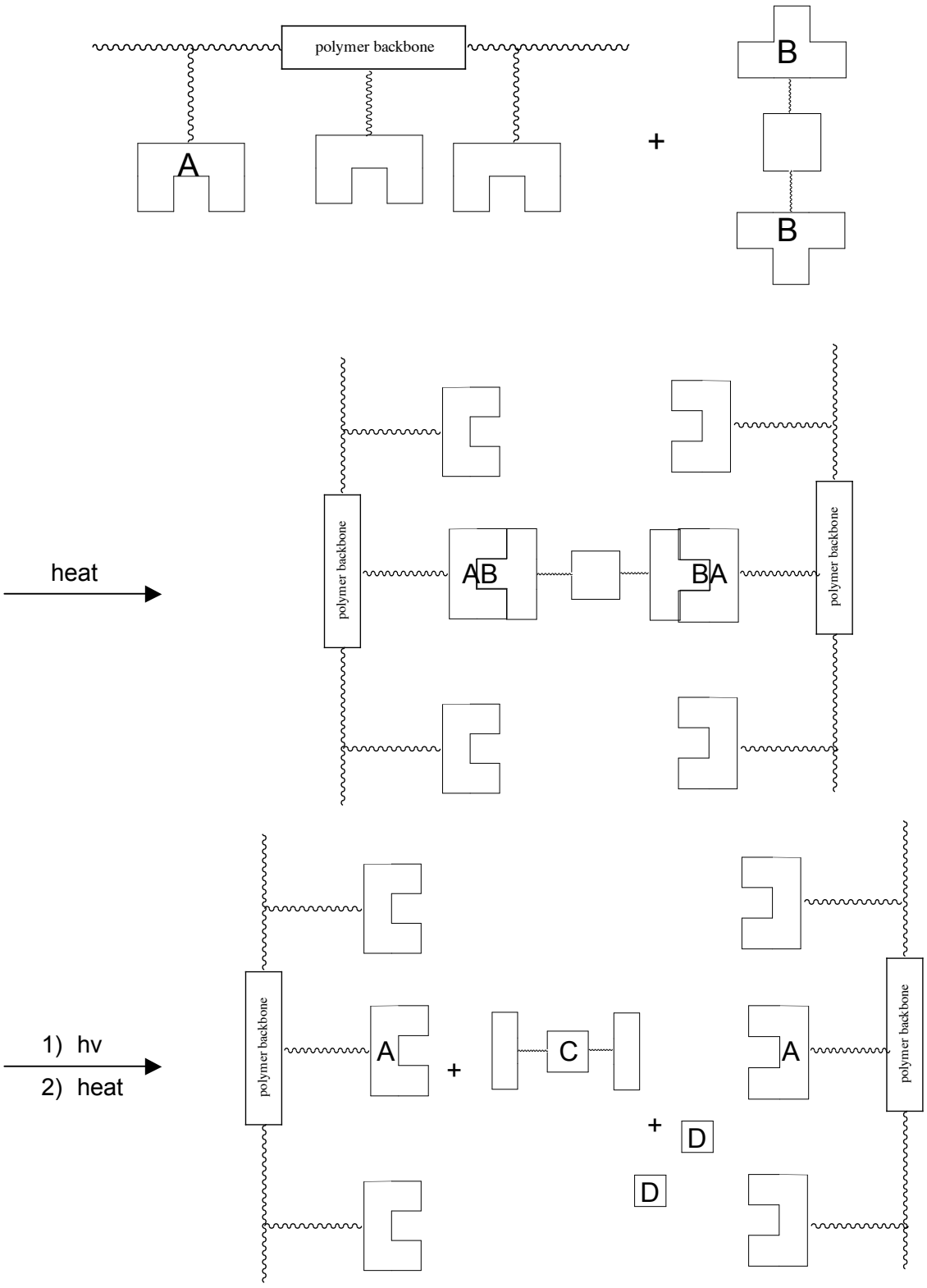


Figure 1. Chemistry of light-sensitive BARCs.

### 3.3 Film properties

Characterization of 193-nm wet BARCs in this series focused on BARC I. Other BARCs (including BARC V) are being developed as part of continuous improvement, with the objectives including improved 193-nm optical properties and/or ever-simpler manufacturability. Selected BARC film properties for both products are summarized in Table 1. The film thicknesses listed were used in generating the EL film stripping, optical density, and percent development data in Table 1. The EL stripping process occurs prior to the exposure step for a BARC and simulates the effects of photoresist solvents on the cured film. Light-exposure of the EL-stripped BARCs in these examples was at 20 mJ using a broadband light source. No covering photoresist was present during the generation of BARC film properties. The post-exposure bake (PEB) parameters were 130°C for 90 seconds. Development was with a 0.26 normal (N) aqueous TMAH solution using a 60-second puddle, a 5-second deionized water rinse, and a spin dry. Half of the wafer was covered during the exposure step, with the covered area allowing an assessment of the effects of developer on unexposed BARC. Coating quality for both BARCs was very good, as were other film properties. All light-exposed and thermally processed areas of the BARCs completely developed with developer, the developer had no significant adverse effects on the unexposed coatings, and the EL stripping test showed complete resistance to the solvent.

Table 1. BARC film properties.

| Identity of Wet BARC | BARC Bake Parameters, °C/sec | Film Thickness, nm | EL Stripping | OD at 193 nm | Development, Exposed Areas | Development, Unexposed Areas |
|---|---|---|---|---|---|---|
| BARC I | 155/60 | 40.1 | -0.87% | 10.8 | -100% | +1.62% |
| BARC V | 165/60 | 42.2 | -0.06% | 14.2 | -100% | -0.25% |

### 3.4 BARC bake window

The BARC bake window is the temperature range in which there is minimal solvent solubility, but total solubility in developer after exposure and PEB. As shown in Table 2, the acceptable processing window for BARC I includes bake temperatures of 145°C through 205°C. At the lower bake temperature of 140°C, development of the exposed BARC is incomplete. An expanded description of bake window for BARC I, in which lithographic performance is considered, will be discussed in section 3.8.

Table 2. Processing window for wet BARC I (a non-lithographic evaluation).

| BARC Bake Parameters, °C/sec | Film Thickness, nm | EL Stripping | Development, Exposed Areas | Development, Unexposed Areas |
|---|---|---|---|---|
| 140/60 | 38.4 | -0.44% | -66.5% | -0.12% |
| 145/60 | 38.6 | -0.22% | -100% | -0.33% |
| 160/60 | 38.6 | -0.03% | -100% | -1.21% |
| 175/60 | 38.1 | +0.57% | -100% | -1.23% |
| 190/60 | 37.8 | +0.51% | -100% | -0.24% |
| 205/60 | 37.0 | +0.12% | -100% | -0.67% |

The data in Figure 2 show the effects of PGME and PGMEA on cured BARC I. The results were similar to those for EL, that is, the product was insoluble in both solvents using BARC bake parameters of 140°C for 60 seconds through 220°C for 60 seconds.

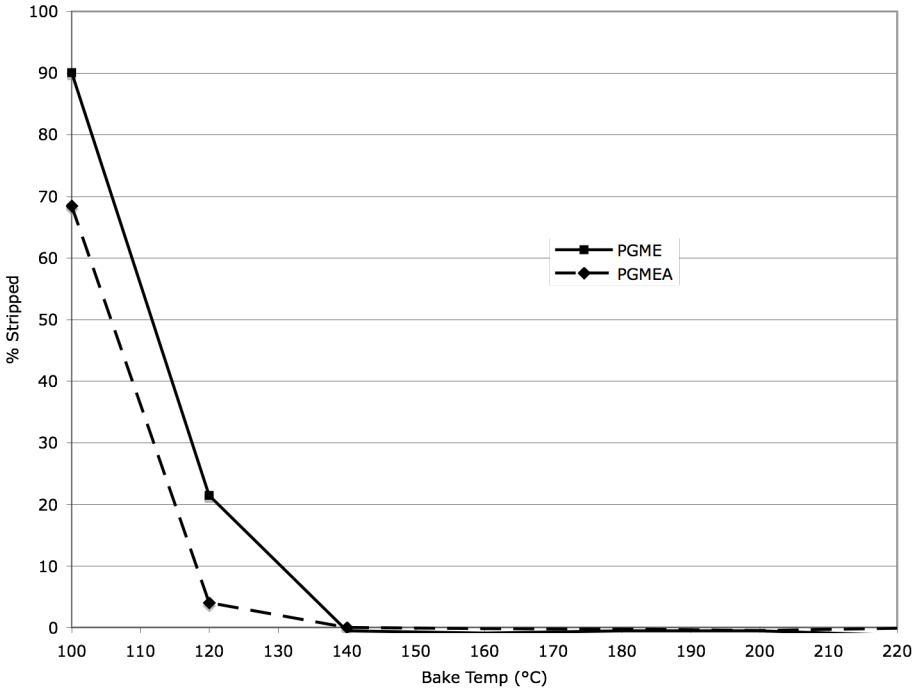


Figure 2. Bake temperature versus stripping of BARC I with PGME and PGMEA.

**3.5 Optical parameters and PROLITH modeling of reflectivity**

The optical constants were measured on a VUV-VASE, with n and k being: 1.66-1.67 and 0.40 for BARC I, and 1.65 and 0.54 for BARC V. These data were used in PROLITH version 9.0 to model the reflectivity curves for the different BARCs on two different substrates: a) silicon and b) 200-nm thick silicon oxide on silicon. The significance of the silicon oxide is that photoresist patterns for an implant mask may be opened on the same substrate.[8] The light source selected for the modeling was conventional–partially coherent, the numerical aperture (NA) was 0.75, and the photoresist was A. The first and second reflectivity minimum BARC thicknesses and the percent reflectance on the two substrates are given in Figure 3. At their respective first reflectivity minimum BARC thicknesses, BARC V (higher k-value product) provides the lowest reflectance for both substrates. At the second reflectivity minimum BARC thicknesses, BARC I (lower k-value product) gives better reflectance control on both substrates. Notably, BARC V gives less than or equal to 3.10% reflectance on both substrates at both first and second reflectivity minimum BARC thicknesses.

The selected PROLITH modeling conditions have some effect on the modeled first and second reflectivity minimum thicknesses. Using annular light and an NA of 0.78 with photoresist A, the first and second reflectivity minimum thicknesses for BARC I are 38 nm and 98 nm, respectively, on a silicon substrate. These values (earliest PROLITH modeling work) most influenced all BARC thicknesses for the lithography studies discussed in Section 3.8.

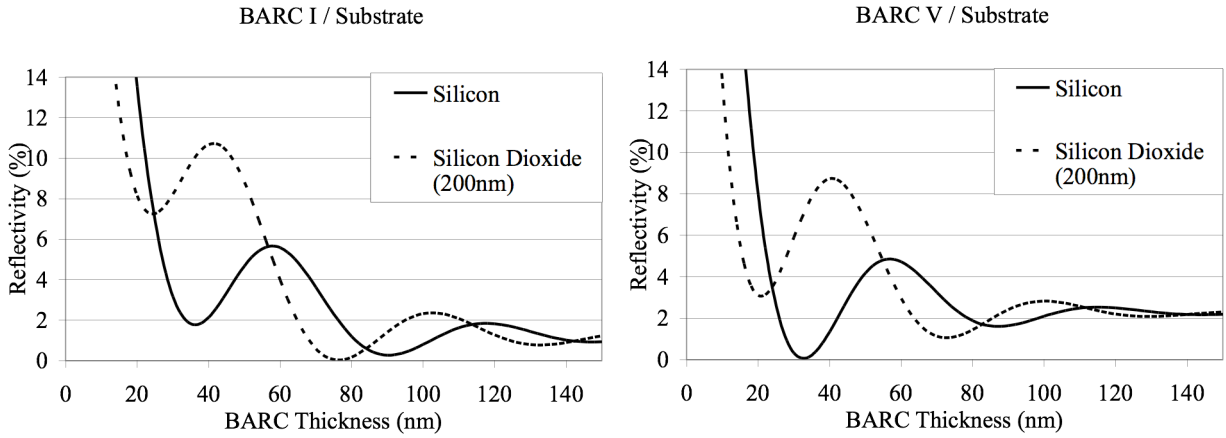


Figure 3. Reflectivity using wet BARCs on two different substrates.

### 3.6 Spin-bowl and solution compatibility

An important property for a BARC is rapid re-dissolution of the dried solids in organic solvents at room temperature. A build-up of polymer on the walls of the spin-bowl might create the need for an unwanted bowl cleaning step. The spin-bowl compatibility test procedure has previously been described, with ≥ 90% re-solubility necessary to pass. There was only one change from the test procedure described in 2001,[7] that is, step 4 was eliminated and a scratch was not made through the BARC. The data are shown in Table 4 for BARCs I and V. BARC I is spin-bowl compatible in all tested solvents, excluding 2-heptanone. BARC V is spin-bowl compatible in solvents (as shown) except 2-heptanone and cyclohexanone. Based on these results, we do not expect any problems with compatibility with EBR systems.

In contrast to spin-bowl compatibility testing, solution compatibility testing is meant to identify potential problems with BARCs precipitating in the spin bowl or drain lines upon mixing with other solvents. About 10 weight % of the BARC was mixed with 90 weight % of a solvent or 193-nm photoresist B at room temperature checking for any precipitation. Then 90 weight % of BARC was mixed with 10 weight % of same photoresist. As shown in Table 4, except for 2-heptanone, both BARCs are compatible with all tested solvents and 193-nm photoresist B. Thus, no precipitation or even haziness occurs on mixing at room temperature.

Table 4. Spin-bowl and solution compatibilities of wet BARCs.

| Solvent/Resist | Spin-bowl Compatibility | | Solution Compatibility | |
|---|---|---|---|---|
| | BARC I | BARC V | BARC I | BARC V |
| PGME | -100% | -100% | yes | yes |
| PGMEA | -100% | -100% | yes | yes |
| Ethyl Lactate | -100% | -100% | yes | yes |
| Cyclohexanone | -100% | -78.9% | yes | yes |
| γ-Butyrolactone | -100% | -100% | yes | yes |
| γ-Butyrolactone/n-Butyl Acetate (70/30 w/w) | -100% | -100% | yes | yes |
| Acetone | -100% | -100% | yes | yes |
| 2-Heptanone | -81.4% | -82.9% | no | no |
| 193-nm Photoresist B | - | - | yes | yes |

### 3.7 Storage stability

A prototype formulation very similar in chemistry to BARC I gave reproducible (±5%) film properties for the length of the entire testing period. The first reflectivity minimum formulation and second reflectivity minimum formulation were tested after 5 and 7 months, respectively. The data are shown in Tables 5a and 5b below, with the spin and bake parameters for the respective BARCs remaining constant throughout the testing sequence. The two formulations differ

only in percent solids and were kept at ambient conditions. The expectation is that other light-sensitive, wet BARCs from this family made from similar chemistries will exhibit comparable room temperature stability. Lithographic performance as a function of storage time is currently under investigation.

Table 5a. Stability of first reflectivity minimum formulation.

| Properties | Film Thickness, Å | EL Stripped Thickness, Å | Development, Exposed/ Unexposed | 193-nm Absorbance | 193-nm OD |
|---|---|---|---|---|---|
| Initial Film Measurements | 394 | 396 | -100%/-0.41% | 0.43 | 10.9 |
| Measurements 5 Months Later | 393 | 395 | -100%/+1.30% | 0.44 | 11.2 |
| Change after 5 Months | -0.25% | -0.25% | 0 /- | +2.33% | +2.75% |

Table 5b. Stability of second reflectivity minimum formulation.

| Properties | Film Thickness, Å | EL Stripped Thickness, Å | Development, Exposed/ Unexposed | 193-nm Absorbance | 193-nm OD |
|---|---|---|---|---|---|
| Initial Film Measurements | 933 | 931 | -100% / +0.48% | 1.06 | 11.4 |
| Measurements 7 Months Later | 946 | 946 | -100% / +1.16% | 1.10 | 11.6 |
| Change after 7 Months | +1.39% | +1.61% | 0 /- | +3.77% | +1.75% |

**3.8 Lithography**

BARC I (38 nm thick) was evaluated for lithographic performance on silicon. Line and space features (150 nm, 1:1) were generated using resist A. Toolset and processing conditions for the lithography data described in Figures 4, 5, and 6 are shown below:

| | FAB 1 | FAB 2 |
|---|---|---|
| Exposure Tool | ASML PASS 5500/1100 | ASML PASS 5500/1150 |
| NA | 0.75 | 0.75 |
| Sigma | 0.89/0.65, dipole illumination | 0.85/0.55, annular illumination |
| Mask | 9% att. PSM | 6% att. PSM |
| PAB/PEB | 105°C for 90 sec | 105°C for 90 sec |
| Developer | OPD5262 (60 sec) | Opti Yield (50 sec) |

Figure 4 shows how the lithographic performance changes over temperature from lithography processed at FAB 1. The BARC bake temperatures were varied using 10°C increments to identify the optimum BARC bake conditions. For each temperature, SEM cross-sections are shown at best focus (+0.2 μm) and best dose (21-22 mJ/cm$^2$). Under these conditions, slightly tapered sidewalls and clean spaces were obtained at bake temperatures equal to or greater than 160°C. Because wet BARCs have the ability to change their performance with different processing conditions, separate tool sets have different optimum process settings. During the course of this research, lithography was performed at two different facilities. At each facility the experimental BARCs were screened against different processing conditions to discover the optimum lithography process.

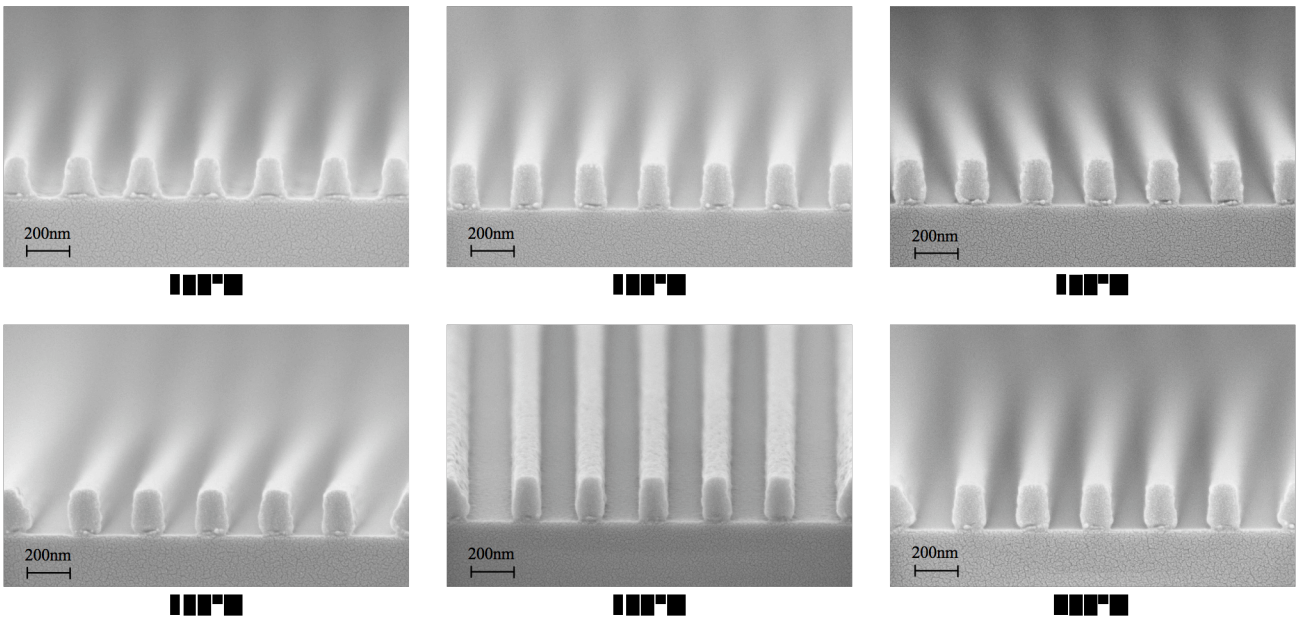


Figure 4. 150-nm L/S (1:1) features on silicon substrate with varying BARC bake temperatures.

It was determined that the best lithographic performance with the resist A and BARC I at FAB 1 was obtained at a BARC bake temperature range of 160°-170°C. Figure 5 shows the SEM cross-sections of the profiles processed at a BARC bake of 160°C and exposed 22mJ/cm$^2$. Across the focus the profiles are slightly tapered, but the spaces are clean.

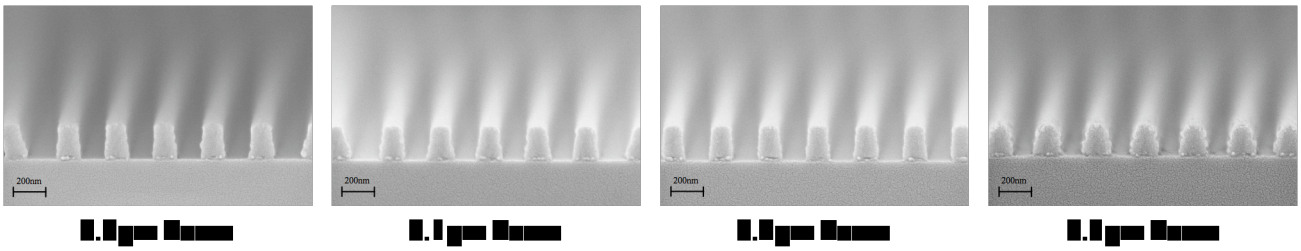

Figure 5. Effect of focus on profiles (160°C BARC bake).

Lithography was also processed at a separate facility, FAB 2. Figure 6 shows SEM cross-sections of profiles from FAB 2 after further optimization of processing conditions. A BARC bake temperature of 155°C and an exposure of 21 mJ/cm$^2$ were used. The profiles are straight and the spaces are clear. Some adjustments were made from FAB 1 to FAB 2. Fine-tuning of the bake temperature at the new FAB to account for a different toolset was made. An adjustment in development time from 60 seconds to 50 seconds was made. Mask types and illumination conditions were also slightly adjusted. It is believed that this improvement in the profiles came from the fine-tuning of these processing conditions, which is similar to targeting a process for a new resist, but in this case, both the BARC and resist processing conditions are tied to each other through bakes. The resist's PAB is a second bake for the BARC, whereas the resist's PEB is also the BARC's PEB and the process must be studied accordingly.

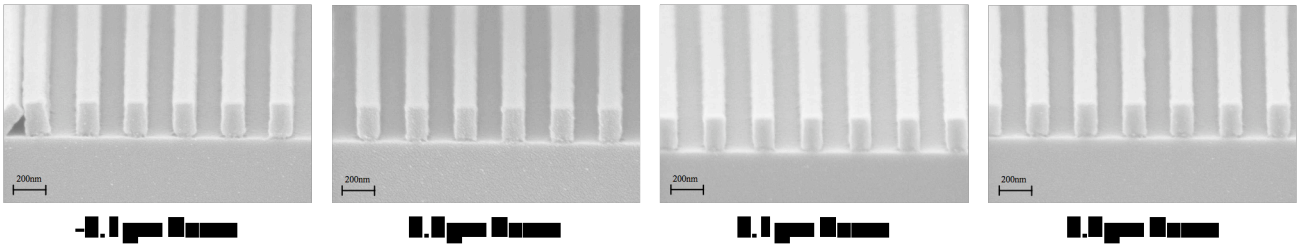

Figure 6. Effect of focus on profiles (155°C BARC bake).

Lastly, as a measure of the lithographic process window for this system, Figure 7 shows the exposure dose latitude that is obtained while targeting for 150-nm L/S (1:1) features from FAB 1. For this example, features within a 10% variation in CD are considered acceptable and are bracketed by dashed lines.

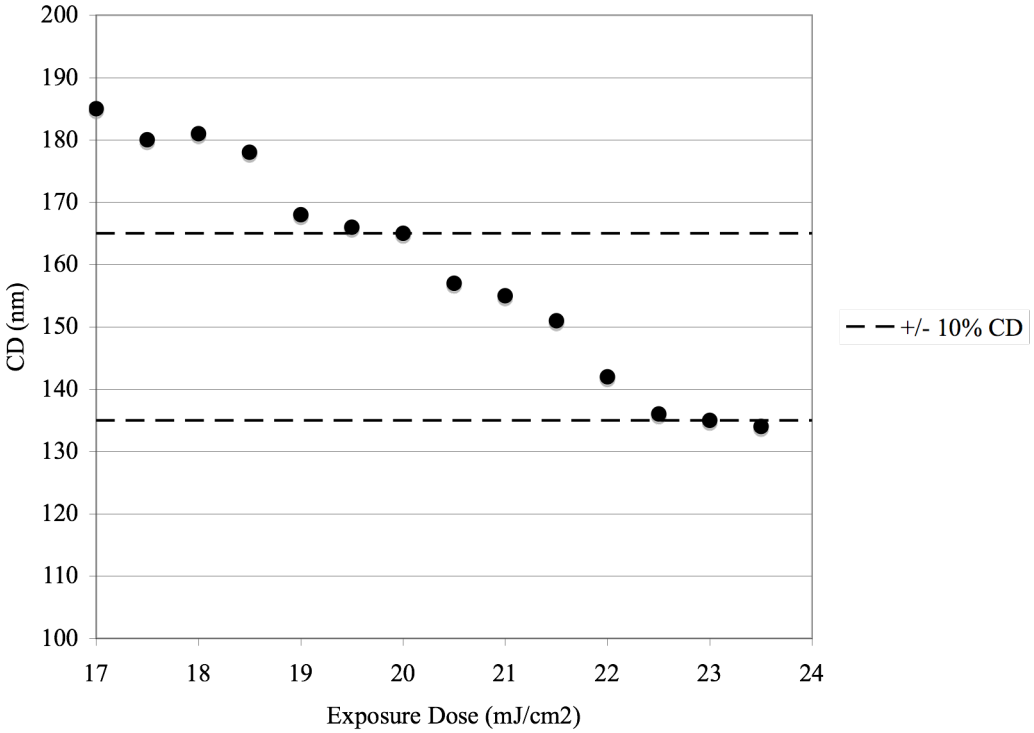


Figure 7. Exposure latitude for resist A and BARC I combination at FAB 1 [150-nm L/S (1:1) features].

## 4. CONCLUSIONS

This paper described progress in developing spin-on, organic, wet BARCs that meet the criteria for 193-nm implant layer applications. The BARCs are sensitive to 193-nm light, are positive-working, and are processed and developed in the same steps as the photoresist. Best-case lithography on a silicon substrate using a 193-nm photoresist A and light-sensitive wet BARC I has given 150-nm L/S (1:1). Line shapes were very good, with optimum BARC bake being 155-170°C for 60 sec. Selected wet BARCs from this chemical family give outstanding reflectivity control, spin-bowl and solution compatibility, and stability for more than 6 months at ambient conditions.

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