A novel 248-nm wet-developable BARC for trench applications

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ABSTRACT
A novel polyamic acid–based, 248-nm wet-developable BARC has been prepared to improve structure clear-out and lessen post-development residue. This material showed an excellent process window and controllable development rates that can be achieved by simply changing the formulation. It is a highly absorbing BARC with $n$ and $k$ values equal to 1.73 and 0.49, respectively. Lithography with this material has shown 180-nm dense profiles with P338 and M230Y. These profiles exhibited minimal undercutting with good clearing between the lines. Clear-out has been demonstrated for 120-nm trenches. Post-development residue of the material was tested at various temperatures and was determined to be 6 Å or less. In addition, sublimation was evaluated.

Key words: wet developable, BARC, 248 nm

1. INTRODUCTION
As critical dimensions continue to shrink in lithography, new materials will be needed to meet the new demands imposed by this shrinkage. For example, new materials will be needed for implant applications. The traditional approach for implant has been to use photoresist with a top anti-reflective coating (TARC). However, TARCs have limited critical dimension (CD) control and do not control reflective notching. BARCs are better choices to improve CD control, reduce reflective notching, and eliminate standing waves. Dry BARCs are unacceptable for implant applications though. The process required to dry-etch a BARC could damage the surface.

To overcome the problems of TARCs and dry BARCs, a wet-developable BARC is needed. Wet-developable BARCs have received interest due to their possibility of improving yields compared to TARCs\textsuperscript{1,2,3}. A wet-developable BARC would provide better CD control and reduce reflective notching compared to a TARC. It also eliminates the need for the plasma etch for dry BARCs. The major requirements of the new material will
be complete clear-out of trench structures and reduced post-development residue. This paper will describe a new wet-developable material for 248-nm lithography.

2. EXPERIMENTAL

2.1 Materials
The materials used in this study were blends of polyamic acid, chromophore, and epoxy crosslinker. The polyamic acid was prepared by reacting 3,3′,4,4′-diphenylsulfone tetracarboxylic dianhydride with a diamine. The chromophore was prepared by reacting trisepoxypropyl isocyanurate with the appropriate aromatic carboxylic acid (Figure 1).

![Figure 1. Synthesis of chromophore.](image)

2.2 Optical Properties
Optical constants, \( n \) and \( k \), were measured with a J.A. Woollam variable-angle spectroscopic ellipsometer (VASE®). The optical constants generated from the VASE were used to create a simulated reflectivity curve with PROLITH version 7.2 software (KLA-Tencor Corp.). The reflectivity curve was used to determine the minimum reflectivity on silicon substrates.

2.3 Dissolution Rates
The film dissolution rates were measured using a dissolution rate monitor (DRM) with a standard 0.26N tetramethyl ammonium hydroxide (TMAH) solution. The DRM used in the experiment was a LithoTech Japan model 790, which uses 470-nm light to detect thickness change and the total develop time. The developer temperature was controlled at 21.2°C using a circulation chiller.
2.4 Sublimation
After the BARC was spin-applied onto the wafer, it was placed onto a metal plate with thermal couple and a funnel-shaped enclosure placed over the wafer (Figure 2). Air was drawn over the wafer at a rate of 2 L/m into an absorption tube. The absorption tube was removed and placed into a methanol wash for 20 hours to remove the sublimate. The methanol solution was then analyzed by HPLC to quantify the amount of sublimate.

![Sublimation apparatus](image)

Figure 2. Sublimation apparatus.

2.5 Profiles
Each sample was evaluated for lithographic performance at IMEC. Each sample was hand dispensed and spin coated to the appropriate thickness (from the reflectivity curve for silicon) and baked for 60 seconds. The BARC was coated with the appropriate photoresist. The photoresist was then processed under the recommended conditions and was then treated with TMAH developer for 60 seconds. Wafers were then cleaved, and cross-sectional SEM micrographs taken at Brewer Science.

3. Results and Discussion
3.1 Material Characterization
3.1.1 Optics
Optics, $n$ and $k$, were measured on a VASE® and determined to be 1.72 and 0.49, respectively. These values were then used in PROLITH simulations to determine the reflectivity curve (Figure 3). In Figure 3, the first minimum, first maximum, and second minimum were determined to be 450, 750, and 1150 Å, respectively. The lowest amount of reflectivity, 0.3%, was observed at 450 Å, which is typical of a highly
absorbing material. Samples were prepared at this thickness for further testing and were designated as BSI.W05041S, BSI.W05041R, and BSI.W05041Q.

3.1.2 Dissolution Rate

Dissolution rates were determined on films of BSI.W05041R that were spin cast on silicon wafers and baked at various temperatures for 60 seconds. The dissolution rate versus temperature curve is shown in Figure 4. In general, the dissolution rate decreased as the temperature increased. However, there was a temperature range of about 10°C, centered at about 190°C, where the dissolution rate changed little. This 10°C degree temperature range creates a broad process window for the BARC and helps with lithography and clear-out from structures [discussed later in this paper].

Figure 3. PROLITH simulations of 248-nm wet-developable BARC with $n$ and $k$ values of 1.72 and 0.49, respectively.

Figure 4. Development rate versus temperature for BSI.W.05041R.
3.1.3 Sublimation

In-house sublimation testing was performed with BSI.W05041R. Samples were prepared by spin application of the material onto a silicon wafer. The wafer was then placed into the chamber and heated, and the sublimate collected. The sublimate was analyzed by HPLC to determine the amount. Figure 5 shows the amount of sublimate of BSI.W05041R at 180º, 190º, and 200ºC to be 0.005, 0.008, and 0.011 µg/nm, respectively. Compared to known low-subliming BARCs, BSI.W05041R was also low subliming. Low sublimation indicates complete attachment of the chromophore to the trisepoxypropyl isocyanurate and lowers the possibility of defects during lithography.

![Sublimation results of BSI.W05041R.](image)

3.1.4 Residue

BSI.W05041R was spin applied to a silicon wafer and was then baked at various temperatures (170º, 180º, and, 200ºC) for 60 seconds. The thickness of the film was measured on the VASE. The material was then developed with 0.26N TMAH for 60 seconds. The thickness of the film was again measured. Figure 6 shows the results. Thicknesses of 2, 3, and 6 Å were observed for 180º, 190º, and 200ºC, respectively. The increase in post-develop residue with temperature is typical of a polyamic acid based material and may be due to more crosslinking of the material at the surface of the wafer. However, the residue was considerably less than that observed for BSI.N0889A. Less residue may lessen problems during implant applications.

3.2 Clear-out and Lithography

3.2.1 Clear-out

Clear-out testing was performed on topography wafers. The wafer was coated with BSI.W05041R, baked, and then developed for 60 seconds with 0.26N TMAH. The wafer was then cross-sectioned and SEM
pictures taken (Figure 7). The initial cross-section was performed on an undeveloped sample. This material showed good fill properties, which was important for reflectivity control. Clear-out testing at bake temperatures of 190º and 200ºC showed complete removal of the material from the trenches. The clear-out performance was excellent and may be attributed to the broad bake window. Material in the trench may have slightly higher heating due to more contact with the silicon wafer and thus more heat transfer. A broader bake window would lessen this effect.

![Figure 6. Post-develop residue testing of BSI.W05041R.](image)

![Figure 7. Clear-out testing of BSI.W.05041R.](image)

3.2.2 Lithography

Lithography was performed on samples (BSI.W05041S, BSI.W0541R, and BSI.W05041Q) at thicknesses of 450, 750 and 1150 Å with JSR’s M230Y resist and TOK’s P338 resist (Figures 8 and 9, respectively). BSI.W05041S and BSI.W05041R showed 1/1 L/S of 180 nm with minimal undercutting. However, BSI.W05041Q was not able to give lines of this size due to the thickness of the material. Since these materials develop in an isotropic manner, a greater amount of undercutting is observed at greater thickness. For BSI.W05041Q, too much undercutting of the profile resulted in line collapse. This material did show 1/1 L/S profiles at 300 nm. Also, a greater amount of undercutting was observed as the thickness of the material increased. This result can also be attributed to an isotropic development.
Lithography was also performed at bake temperatures of 185°, 190°, and 195°C. Temperature effects were greater as the thickness of the material increased (Figure 10). For BSI.W05041S, bake temperature had little effect on undercutting. In contrast BSI.W05041Q showed a significant dependency on temperature with undercutting occurring more at lower temperatures.

![Figure 8. Lithography with BSI.W05041S, BSI.W05041R, and BSI.W05041Q with P338 at 1/1 L/S of 180, 180, and 300 nm, respectively.](image)

Figure 9. Lithography with BSI.W05041S, BSI.W05041R, and BSI.W05041Q with M230Y at 1/1 L/S of 180, 180, and 300 nm, respectively.

### 4. Conclusion

A new wet-developable BARC, BSI.W05041R, has demonstrated improved clear-out and less residue compared to previous polyamic acid materials. This improvement was attributed to an increase in bake latitude, which was observed in the develop rate versus temperature curve. Lithography with this material showed minimal undercutting with complete clearing between the profiles. A bake temperature effect was observed for the material; as temperature increased, more of a foot within the BARC was observed. Also, the material exhibited greater undercutting as the material thickness increased due to isotropic development. The improved properties of this material make it attractive for applications where clearing out structures is difficult or for applications where residue is problematic.
5. References

