Hybrid BARC approaches for FEOL and BEOL integration

Willie Perez\(^a\), Stephen Turner\(^a\), Nick Brakensiek\(^a\), Lynne Mills\(^b\), Larry Wilson\(^b\), Paul Popa\(^b\)

\(^a\)Brewer Science, Inc., 2401 Brewer Dr., Rolla, MO 65401
\(^b\)The Dow Chemical Company, 1712 Building, Midland, MI 48674

ABSTRACT

Spin-on bottom anti-reflective coatings were introduced to the semiconductor industry about 20 years ago to help control substrate reflectivity, improve critical dimension (CD) control, and, most importantly, improve depth of focus window, thus improving throughput and yields. Bottom anti-reflective coating (BARC) materials are either inorganic or organic in nature. Inorganic BARCs are chemical vapor deposition (CVD) films that work on the principle of destructive interference to eliminate reflectivity and demand tight thickness control in the BARC layer. In contrast, organic BARCs are generally spin-on polymeric materials that reduce substrate reflectivity by absorbing exposure radiation to provide greater latitude in thickness control. As an added benefit, organic spin-on BARCs also provide a level of planarization efficiency prior to photoresist deposition to improve depth of focus and process window in the photolithography step.

As feature sizes continue to shrink, etching becomes very challenging due to thin ArF photoresist (PR) layers, which are much less etch resistant compared to KrF photoresists. The reduced thickness, as well as the reduced etch resistance, of the PR makes it nearly impossible to use the PR as both an imaging and a pattern transfer layer. This has led to the development of a new class of spin-on “hybrid” BARC materials which not only have improved etch selectivity to the PR due to inorganic functionality but also have the absorbing properties, and hence offer greater process latitude. Hybrid BARC (H-BARC) materials enable the BARC layer to act as both an anti-reflective coating and as a pattern transfer layer in standard etch-back integration schemes. Due to the polymeric functionality associated with H-BARCs, these materials have exceptional gap-fill and planarization properties and can also be used in via-first dual damascene applications where similar etch characteristics between interlayer dielectric materials and the via-fill BARC enable better CD control.

This paper will focus on the benefits of ENSEMBLE\(^*\) ARC\(^*\) materials, a new class of spin-on hybrid BARC materials, which can be used in either standard BARC applications or in via-first dual damascene applications which require that the BARC act both as an anti-reflective coating and as a via-fill material to assist in CD control during trench etch processes. This paper demonstrates lithography with 193-nm resists, resist compatibility, via-fill performance, optical properties, and etch rates with different plasma recipes.

1 INTRODUCTION

Bottom anti-reflective coatings (BARCs) were developed about 20 years ago to help control reflections from the substrate, improve critical dimension (CD) and most importantly, improve the depth of focus. During that time, chip manufacturers had two choices of BARCs, either spin-on organic coatings or BARCs deposited by chemical vapor deposition (CVD). Each material has respective advantages and disadvantages. Spin-on BARCs have excellent planarizing properties and optical properties but etch only slightly faster than the photoresist. CVD BARCs are conformal in nature, have limited optical property ranges, and exhibit excellent etch selectivity to photoresist.

This paper will discuss a new spin-on hybrid BARC (H-BARC) that combines the properties of both CVD and organic BARCs. These include excellent planarizing properties for via-fill or gap-fill approaches and etch selectivity to the photoresist that rivals that of CVD BARCS. The advantages of H-BARC will be shown by looking at the material

---

\(^*\) Trademark of The Dow Chemical Company
\(^\#\) Trademark of Brewer Science, Inc.
properties such as shelf life, optical tuning capability, dry-etch selectivity, and wafer cleaning. Photolithography process windows and resolution capabilities that are comparable to current organic BARCs will be demonstrated. The planarizing properties of the material will be demonstrated along with the via-first dual damascene integration through the trench etch. Wafer-coating processes were also explored and coat process windows were found to be compatible with 300-mm wafer processes.

2 RESULTS AND DISCUSSION

2.1 ENSEMBLE ARC Chemistry/General Properties Sections
ENSEMBLE ARC formulations consist of an organosilicate copolymer in a PGMEA (1-methoxy-2-acetoxypropane) solvent system. The organic functionality was chosen to enable tuning of the optical properties of cured films to meet application-specific requirements.

ENSEMBLE ARC formulations can be spin coated on standard (photolithography) spin tracks and hot plate cured between 175-425°C with no degradation in optical characteristics. Formulations can be selected over a k-value range from 0.15-0.75, with thicknesses ranging from <10 nm to 1000 nm.

![Figure 1. ENSEMBLE ARC polymer chemistry.](image)

2.2 Extinction Coefficient and BARC Reflectivity
The extinction coefficient of a BARC material generally depends on the loading of chromophore that is in the material. While reflectance that approaches 0 is ideal, a good target for front-end-of-line (FEOL) and back-end-of-line (BEOL) applications at 193 nm is having reflectance less than 1%. The extinction coefficient for ENSEMBLE ARC films can be tuned from $k_{193} \sim 0.15$ – $k_{193} \sim 0.75$. Reflectivity curves (Figure 2) using PROLITH/2 were generated for both first- and second-minimum films on silicon where $k_{193}$ was 0.53 and 0.36, respectively.

![Figure 2.](image)
For various 193-nm applications, BARC materials have the potential for coating substrates other than silicon, for instance, hardmask materials such as silicon oxynitride (SiON) and α-carbon. Tornado plots using PROLITH/2 were generated for an ENSEMBLE ARC film with a $k_{193} \approx 0.36$ with varying thickness of each hardmask material. Figures 3 and 4 show the maximum and minimum reflectivity of the ENSEMBLE ARC film over SiON and α-carbon, respectively.

Figure 3.

Figure 4.
2.3 Wet Etch
ENSEMBLE ARC films were spin coated onto four 8-inch wafers using spin speeds to give film thicknesses between 3000-4500 Å. After spin coating, wafers were hot plate baked at 150°C, 175°C, 200°C, and 225°C in an ambient environment. Film thicknesses were measured using a Nanospec 210 interferometer. A series of wet clean chemistries from Air Products, EKC Technology, Inc., and Mallinckrodt Baker was used in the wet clean experiments. Nominal 1-inch pieces of coated wafer were placed in the clean chemistries for times ranging from 30 seconds to 12.5 minutes. After etching, films were quenched in deionized water and dried with nitrogen. The film thicknesses were remeasured and etch rates were calculated.

BARC films must be able to be readily stripped during rework processes without damage to underlying structures. In addition, in via-first integration schemes BARC etch residue must be removed after dry-etch steps. The wet-etch rates of ENSEMBLE ARC films were measured in a range of wet-etch chemistries. The most promising wet-etch chemistries are shown in Table 1, along with comparative etch rates for materials in the integration stack.

<table>
<thead>
<tr>
<th>Etch Chemistry</th>
<th>Etch Temperature, °C</th>
<th>ENSEMBLE ARC Etch Rate, Å/min</th>
<th>Inorganic Low K Etch Rate, Å/min</th>
<th>Cu Etch Rate, Å/min</th>
<th>Al Etch Rate, Å/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACT® NE-891</td>
<td>22</td>
<td>330</td>
<td>&lt;1-35</td>
<td>4</td>
<td>11</td>
</tr>
<tr>
<td>EZStrip 5231</td>
<td>55</td>
<td>1535</td>
<td>&lt;1-27</td>
<td>&lt;1</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>EZStrip 6011</td>
<td>22</td>
<td>495</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EZStrip 6011</td>
<td>30</td>
<td>1325</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EZStrip 6011</td>
<td>65-75</td>
<td>&gt;125000</td>
<td>&lt;1-8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALEG®-3102</td>
<td>85</td>
<td>440</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CLk™-8882 (10:1)</td>
<td>65</td>
<td>135</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XM-2682</td>
<td>45</td>
<td>&gt;2600</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKC5253</td>
<td>50</td>
<td>875</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EKC5103</td>
<td>50</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 shows the impact of the BARC film age on the wet-etch rate in ACT NE-89. These data show that the wet-etch rates are independent of the age of the BARC films. Similar results were observed for other chemistries listed in Table 1. Figure 6 illustrates the impact of the ENSEMBLE hot plate bake temperature on the wet-etch rate. This figure shows some slight dependency on the bake temperature, however, over the recommended hot plate bake temperature range for the products, the etch rate is essentially constant.

1 Air Products
2 Mallinckrodt Baker
3 EKC Technology, Inc.
4 at 25°C
ENSEMBLE ARC Etch Rate in ACT NE-89

Figure 5.

ENSEMBLE ARC Etch Rate in ACT NE-89

Figure 6.

2.4 Dry Etch
ENSEMBLE ARC films were spin coated onto 8-inch wafers at 1000 rpm. The films were hot plate baked at 200°C for 2 minutes in an ambient environment. Films thicknesses were measured using a Nanospec 210 interferometer. Wafers were sectioned into nominal 3-inch pieces prior to etching. Etch rates in CF\textsubscript{4}, O\textsubscript{2}, and CF\textsubscript{4}/O\textsubscript{2} blends were determined using a Tegal 903E etch tool operating between 350-500 W, 4-100 sccm, 170-350 mTorr, and 21°C. Films were etched for 15 and 60 seconds, after which film thicknesses were remeasured.
Etch rates for ENSEMBLE ARC 1st and 2nd minima films were measured as described above. For comparison, Black Diamond, Coral, SiLK J, SiLK S, porous SiLK, JSR ARF AR1221J, TOK TARF-P6111 ME, thermal oxide and SiN films were also etched under the same conditions. Figures 7, 8, and 9 show the relative etch rates of the materials tested and show that the ENSEMBLE ARC films etched similarly to the inorganic films in the study in all etch environments. In oxygen the etch rates of ENSEMBLE ARC and the inorganic films tended to be slightly higher than the organic films. The etch rate of ENSEMBLE ARC 1st and 2nd minima films were 265 Å/min and 180 Å/min after 15 seconds of etching. After etching for 60 seconds in oxygen, no further reductions in film thickness were observed, which indicated that passivation of the ENSEMBLE ARC films in oxygen was complete after 15 seconds.

![Figure 7](image1.png)

**Figure 7.**

![Figure 8](image2.png)

**Figure 8.**
2.5 Coat Defects
A design of experiment (DOE) was developed to characterize the coating properties and define a low-defect dispense process for the ENSEMBLE ARC36-80 material on 300-mm wafers. The thickness was targeted to be 80 nm at 1500 rpm. The factors tested were dispense volume, dispense rate, wafer spin speed during dispense, exhaust of the coat bowl, and the pump reload rate. Factor settings in the DOE are found in Table 2. The coat track used in this experiment was an ACT12 and an SP1 scanning 0.2 μm size and larger.

<table>
<thead>
<tr>
<th>Factor</th>
<th>DOE Settings (Low/High)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispense Volume (mL)</td>
<td>0.5 / 2.0</td>
</tr>
<tr>
<td>Dispense Rate (mL/sec)</td>
<td>0.5 / 2.0</td>
</tr>
<tr>
<td>Dispense Speed (rpm)</td>
<td>500 / 2500</td>
</tr>
<tr>
<td>Reload Rate (mL/sec)</td>
<td>0.1 / 1.2</td>
</tr>
<tr>
<td>Exhaust (MPa/min)</td>
<td>10 / 25</td>
</tr>
</tbody>
</table>

Once the DOE was completed and analyzed, the factors that impact the defects the most are dispense volume, dispense rate, wafer speed, and reload rate. The exhaust has a small effect indicated by almost straight lines on the modeled results. The results were modeled and then optimized for a low defect coat process. The results indicate a high dispense speed, a high volume, low dispense rate, and high reload rate. Figures 10, 11, and 12 show the modeled results of the DOE.
Using the modeled results, wafers were coated using a “good” and a “bad” process. The results are shown in Table 3.

Table 3.

<table>
<thead>
<tr>
<th></th>
<th>Dispense Volume (mL)</th>
<th>Dispense Rate (mL/sec)</th>
<th>Dispense Wafer Speed (rpm)</th>
<th>Pump Reload Rate (mL/sec)</th>
<th>Exhaust (Mpa/min)</th>
<th>Results (3 wfr avg ± range/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Good” X</td>
<td>2.0</td>
<td>0.5</td>
<td>2500</td>
<td>1.2</td>
<td>25</td>
<td>13±2</td>
</tr>
<tr>
<td>“Bad” O</td>
<td>0.5</td>
<td>2.0</td>
<td>500</td>
<td>0.1</td>
<td>25</td>
<td>741±38</td>
</tr>
</tbody>
</table>
With almost two orders of magnitude difference in defect count depending on the process, optimization is necessary for specific production environments, but the capability for production-worthy spin-coat processes has been demonstrated.

### 2.6 Spin-Bowl Compatibility

It is desired for ENSEMBLE ARC films to be spin-bowl compatible with EBR and common photoresist solvents to prevent precipitation in the spin bowl and drain lines. ENSEMBLE ARC was coated on a silicon wafer and allowed to dry for various amounts of time in ambient clean room conditions. The film thickness was measured, and then the wafer was immersed in various solvents for 3 minutes and spun dry. The wafer was measured for thickness again to determine loss of film. Figure 13 shows the results of film lost in various solvents with respect to time sitting in ambient clean room condition.

![ENSEMBLE ARC Spin-Bowl Compatibility](image)

Figure 13.

### 2.7 Via-Fill and Poly Line Testing

This BARC can be used in via-first dual damascene applications where similar etch characteristics between interlayer dielectric materials and the via-fill BARC enable better CD control. The via-fill properties of this BARC were tested over a range of via diameters (0.22-0.6 μm), with a depth of 0.7 μm. The via-fill properties were also tested over a variety of spin speeds (1000-4000 rpm). Due to the polymeric functionality associated with this BARC, the material exhibits exceptional gap-fill and planarization properties. This BARC was tested for percent planarity over a range of poly line depths. See Figure 14.
Figure 14.
2.8 Lithography
Lithographic performance can be one of the most important factors when selecting a BARC. The BARC must be compatible with a variety of resist platforms to provide adequate imagibility and depth of focus. In Figure 15, ENSEMBLE ARC films are shown below over a variety of resist platforms.

![Figure 15](image1)

2.9 Integration
ENSEMBLE ARC has shown the desired properties for both FEOL and BEOL applications. While each piece of data is important, full integration of process flows is essential. The integration stack that was used for testing was SiON over Black Diamond. Once the vias were printed, etched, and subsequently cleaned, ENSEMBLE ARC36-80 was coated for both full-fill and partial-fill applications. The coating properties can be seen in the cross-sections in Figures 16 and 19. The next process step was to apply resist for printing the trench. Cross-sections were taken after this process step again for both full-fill and partial-fill applications and can be seen in Figures 17 and 20. The next step in the process flow was trench etch. Figures 18 and 21 are cross-sections after trench print in which an un-optimized etch gas recipe was used. Wet cleaning module optimization is ongoing.

![Figure 16](image2)

![Figure 17](image3)

![Figure 18](image4)
Figure 22 demonstrates the use of ENSEMBLE ARC as a replacement for SiON and a standard organic ARC in FEOL patterning applications. The hardmask and anti-reflective properties of ENSEMBLE ARC are evident in this series of micrographs. This combination of hardmask and BARC into a single spin-on film leads to a simplified, lower cost integration scheme.
3 SUMMARY

ENSEMBLE ARC films represent a new class of spin-on hybrid BARC materials that are well suited for both FEOL and BEOL applications. These films can be used in both blanket film applications to control substrate reflectivity and in applications where via-fill and planarization are required. In addition, the hybrid nature of these films provides for improved etch selectivity between the BARC and photoresist, allowing for dual functionality during integration. ENSEMBLE ARC formulations also have excellent shelf lives, are compatible with leading 193-nm photoresists, exhibit stable film properties as a function of film age, and are tunable to allow for reflectivity control across key substrates.

4 ACKNOWLEDGMENTS

The authors would like to thank the following for their hard work and many contributions:

- Brewer Science, Inc.
- The Dow Chemical Company
- SILKNet Alliance℠ Partners
  - Air Products - ACT
  - ATMI
  - Dupont EKC Technology
  - SEZ Group
  - Tokyo Electron Limited
- Mallinckrodt Baker