Recent Progress in Organic Bottom Anti-reflective Coatings

Xie Shao¹, Jim Meador¹, Shree Deshpande¹, Rama Puligadda¹, Kenichi Mizusawa² and Shinya Arase²

¹: Brewer Science, Inc., 2401 Brewer Drive, Rolla, MO 65401, USA
²: Nissan Chemical Industries, Ltd., 722-1 Tsuboi-cho Funabashi-shi Chiba 247-8507, Japan

The primary benefits of bottom anti-reflective coating (BARC) in photolithography are focus/exposure latitude improvement, enhanced CD control and the elimination of reflective notching. As the semiconductor industry demands higher chip functionality, the drive to reduce linewidths and increase die density per wafer is intense. The introduction of BARC technology can postpone the necessity to introduce new equipment needed for these shrinks by enhancing the capability of existing equipment, thus reducing product development time and also eliminating qualification of new material and tool sets. This paper reviews substrate reflectivity, and discusses and reports on material requirements for advanced organic BARCs. Some of the new BARC products based on the design requirement will also be discussed.

Key words: optical lithography, reflections, dual damascene, BARC

1. Introduction

The semiconductor industry’s technology-driven transition to 0.13µm and 0.10µm is expected to happen within a few years. Optical lithography is still the desired approach due to its cost effectiveness. Significant progress in photoresists, optical proximity correction and phase shift masks now allow an extension of 248nm Deep Ultraviolet (DUV) lithography beyond 180nm production. In the past few years, tremendous emphasis and resources have been applied to developing 193nm technology. The target is to bring the 193nm technology to the marketplace for the 130nm or below in production [1-5]. Some device companies are now considering the use of 193nm dual damascene technology as their first 193nm application. As feature sizes continue to shrink, more devices can be packed onto a die. This decreases gate delays, which, in turn, create higher speed circuits. At the same time, this shrinkage results in higher line resistance and line-to-line capacitance. It also results in increased interconnect delays that could cause a decrease in device speed. [6]. Copper and low k dielectric materials have thus been introduced in the industry to address the above-mentioned issues. Because of the nature of copper, dual damascene process is required to avoid an etch procedure to incorporate copper in circuits.

Several potential problems may influence the introduction of new technologies into the semiconductor industry. First, CD control becomes increasingly critical as feature size continues to shrink. Tight control of reflectivity becomes more important than ever. While BARCs have been widely used in the semiconductor industry, more detailed BARC/resist compatibility will continue to challenge the chemists and engineers at both BARC and resist companies. Secondly, post development defects are a serious concern for device fabrication. This problem will directly affect output and cost. Resist poisoning from the low k dielectric process and etch-through in the dual damascene process are two critical problems currently present in the semiconductor industry.
2. Substrate Reflectivity

Figure 1 illustrates a typical substrate reflectivity curve of a BARC layer based on Prolith simulation results [7].

The variation of energy interacting with the resist is a function of the resist thickness and substrate reflectivity. The substrate reflectivity curve from the BARC is a combination of three components [8], represented by R1 - R3 in Fig. 2.

\[ R_1 \sim \exp(-2k_\text{b}T_b) \]

The first component, R1, is the result of the absorption from the BARC. It exponentially decreases at twice the thickness of the BARC [as the light passes through it twice; once into and once back from the substrate].

\[ R_2 \sim \exp(-2k_\text{b}T_b) \sin(4\pi n_\text{b}T_b/(\lambda+\phi)) \]

R2, the second component, represents a periodic function due to interference effects within the BARC film, where the period is a function of the real component of the refractive index. The amplitude is related to the energy absorbed within the BARC film.

R3 is the component that never penetrates into the BARC based on the difference in refractive index between the resist and the BARC. This component is independent of the BARC thickness.

\[ R_3 = \frac{(n_\text{b}-n_\text{r})^2 + (k_\text{b}-k_\text{r})^2}{(n_\text{b}+n_\text{r})^2 + (k_\text{b}+k_\text{r})^2} \]

It can be seen that an increase in the absorbance of the BARC \([k_\text{b}]\) will cause a decrease in the reflectivity \(R_1\) and smaller amplitude in the periodic oscillation \(R_2\). However, if the difference between the resist and BARC refractive index increases, \(R_3\) will increase and therefore the background reflectance will also increase, resulting in a high percentage of reflectivity in the thick version of the BARC.

3. Materials Design

BARC compositions are required to perform three functions: (1) provide a uniform, defect-free coating over the substrate; (2) offer high absorbance at the exposure wavelength so as to reduce swing effects and reflective notching; and (3) etch faster than the photoresist.

In general, spin-on organic BARC is a liquid formulation comprised of the following main components: a polymeric binder, a light absorbing material - either attached to the polymer binder or not, and a solvent system. Polymers selected for BARC coatings must have sufficient solubility in their formulation. They should be thermally stable, have good adhesion to the substrate, be inert to the solvent in the BARC formulation and to the subsequent processing solvents, and exhibit high plasma-etch rates. The light absorbing material (chromophore) must offer high absorbability for the given wave length, high etch rate, and inertness to both BARC and subsequent processing solvents, and exhibit low or no sublimation. The solvent system must be environmentally safe, inert to the coating system, and should have a high flash point.
3.1 Materials design for dual damascene application

The dual damascene (DD) process was implemented in manufacturing semiconductor devices a few years ago [9-13]. Damascene is a means of patterning metal lines wherein metal is deposited into features (canal like trenches and/or vias) etched into the dielectric. This contrasts with the more commonly used process of etching lines in thin metal film and adding a dielectric overcoat. There are four variations of the DD process that have been developed [14], trench-first, via-first, buried etch mask, and buried etch stop. Among them, the via-first approach has drawn much attention because of its reduced number of process steps and improved photolithography process window [15]. The via-first process requires a layer of via fill material to be applied beneath the photoresist layer. The primary function of this via fill material is to act as an etch block at the base of the vias to prevent over etching and punch through of the bottom barrier layer during the trench etch process. However, such material also helps to planarize the substrate and may limit back reflection from the substrate as well, helping to control the critical dimension of the printed features.

A good via fill material should not only exhibit conventional thin film coating properties, but also void free filling, sufficient top coverage, low dimple depth and less bias between iso/dense vias. The coating and via fill qualities are controlled by several important factors such as molecular structure, molecular weight, viscosity of formulation, solvent system, and baking conditions. It is obvious that new BARCs with capabilities in both top coverage and good via fill will be excellent for DD applications.

Materials design for high resolution DUV

The three most important parameters for designing next generation DUV BARCs are: (1) thickness of the BARC layer at which maximum reflectivity control could be achieved, (2) etch rate of the BARC layer with respect to photoresists designed for 150nm and 130nm nodes, and (3) ease of manufacture.

The real refractive index (n) for typical BARC compositions ranges from 1.45 to 1.7 while the imaginary refractive index (k) can vary from 0.35 to 0.5. Simulation using Prolith for substrate reflectivity shows that high n and k values allow us to achieve good reflectivity control at much thinner films.

The thickness of the bottom anti-reflective coating (BARC) and its etch rate relative to the photoresist determine how much resist is lost during the dry etch step. In order to minimize resist loss during BARC etch, BARC compositions that have high etch selectivity and/or high n with optimized k are desired [16].

3.2 Materials design for 193nm technology

Although 248nm lithography will be used across the board for the first generation of 0.13µm devices, 193nm systems must be adopted soon thereafter. With the performance seen today, the second and third generations of 0.13µm devices will have a substantial number of critical layers that will require 193nm for gate, contact and via patterning.

While resist companies are working very hard to address issues like etch resistance, better adhesion and line-edge roughness, development of a BARC with high etch rate and broad compatibility with 193nm resists is the main challenge for BARC companies. Much effort has been put into the selection of polymer backbones and chromophores with high etch selectivity to resist. A big challenge for BARC companies is the optimization of BARC/resist compatibilities. Resist companies tend to put a new resist into the marketplace quickly with short life expectancy, and then change to a subsequent generation or newly modified resist.

4. Experiments and results

4.1 DUV52 and DUV54 for dual damascene application

4.1.1 Chemistries

Based on our in-house technology, two planarizing DUV BARCs, DUV52 and DUV54, have been designed and developed for dual damascene application. DUV52 and DUV54 have the same polymer backbone; however they differ in crosslinkers. Low molecular weight polymer was used to ensure maximum material flow before cross-linking. An additive was also included in the formulation to enhance the polymer flow property. DUV52 is designed to have good compatibility with ESCAP resist while DUV54 is good for an acetal-type of resist. The chemical structure of the polymer used for both is shown in Figure 3:
4.1.2 Basic properties
Table 1 lists some basic properties of DUV52 and DUV54. As shown in Figures 4 and 5, both DUV52 and DUV54 show good full fill or partial fill, void-free properties in vias with diameters of 0.20µm and depth of 1.0µm. In addition, they provide sufficient top coverage and small thickness bias of isolated and dense vias (shown in Table 2 and Figures 4 and 5), and offer good resist compatibility at feature sizes less than 0.2µm (Figures 6 & 7). Figure 8 is the reflectivity curve of DUV52 and DV54.

Table 1: Basic Properties of DUV52 and DUV54

<table>
<thead>
<tr>
<th></th>
<th>MW</th>
<th>n</th>
<th>k</th>
<th>Etch rate*</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUV52</td>
<td>8,500</td>
<td>1.55</td>
<td>0.45</td>
<td>1.2</td>
</tr>
<tr>
<td>DUV54</td>
<td>8,500</td>
<td>1.48</td>
<td>0.45</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* HBr/O2: Selectivity to DUV photoresist.

Table 2: Via filling properties of DUV52 and DUV54

<table>
<thead>
<tr>
<th>BARC</th>
<th>Top thickness, Å</th>
<th>Dimple depth, Å</th>
<th>Top iso/dense bias, Å</th>
<th>Maximum Topography, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Iso</td>
<td>Dens</td>
<td>Iso</td>
<td>Dens</td>
</tr>
<tr>
<td>DUV52 0.2µm</td>
<td>1460</td>
<td>360</td>
<td>1250</td>
<td>1100</td>
</tr>
<tr>
<td>DUV54 0.2µm</td>
<td>1350</td>
<td>550</td>
<td>600</td>
<td>800</td>
</tr>
</tbody>
</table>

Fig. 4. DUV52 fill 0.20µm via diameter and 1.00µm depth holes

Fig. 5. DUV54 fill 0.20µm in via diameter and 1.00µm depth holes

Fig. 6. The profiles of resist B on DUV52 at 0.13 µm L/S at best focus. Resist thickness: 480nm.

Fig. 7. Profiles of resist C on DUV54 at 0.20µm feature size (Resist thickness: 400nm; Exposure tool: NA=0.63 Sigma=0.75; BARC thickness: 1386Å; Exposure dose: 20mJ/cm²).
Figure 9 and 10 show the via fill and lithographic performances of one of our 193nm dual damascene BARC candidates: fast etch application. The polymers used in DUV64 and DUV74 have combined properties of: 1) a polymer binder, 2) a chromophore having high absorbance at 248nm wavelength, and 3) a crosslinker. A small amount of catalyst is required to catalyze the cross linking reaction. Figure 11 shows the schematic structure of the polymer.

**Chemistries**

Two materials have been developed for next generation DUV application. They are DUV64 and DUV74. DUV64 and DUV74 consist of the same co-polymers but are different in building block ratios. DUV64 is designed for use in its first minimum thickness, and DUV74 is designed for fast etch application. The polymers used in DUV64 and DUV74 have combined properties of: 1) a polymer binder, 2) a chromophore having high absorbance at 248nm wavelength, and 3) a crosslinker. A small amount of catalyst is required to catalyze the cross linking reaction. Figure 11 shows the schematic structure of the polymer.

**Basic properties**

Some of the properties of these two products are shown in Table 3, in comparison with DUV44:

<table>
<thead>
<tr>
<th></th>
<th>MW</th>
<th>n</th>
<th>k</th>
<th>Petcha*</th>
<th>1 min.*</th>
<th>2 min.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUV64</td>
<td>30000</td>
<td>180</td>
<td>0.64</td>
<td>430</td>
<td>350</td>
<td>520</td>
</tr>
<tr>
<td>DUV74</td>
<td>30000</td>
<td>210</td>
<td>0.67</td>
<td>480</td>
<td>350</td>
<td>580</td>
</tr>
<tr>
<td>DUV44</td>
<td>69000</td>
<td>146</td>
<td>0.42</td>
<td>365</td>
<td>600</td>
<td>1400</td>
</tr>
</tbody>
</table>

* HBr/Ox, selectivity to DUV resist.
** <2% reflectivity on Poly silicon.

In Table 3, both DUV64 and DUV74 show high etch rates in gases that are typically used for substrate etch, making an extra BARC etch step...
unnecessary. Figure 12 shows the significant improvement in etch selectivity of DUV64 and DUV74 as compared to DUV44, which is the fastest etching 248nm BARC currently produced by Brewer Science.

3.3.1 Optical properties:
The new BARCs described here have real refractive indices ranging from 1.90 to 2.10. Coupled with these high n values are k values, which can range from 0.35 to 0.51. As shown in Figure 13, the first reflectivity minimum for DUV64 and DUV74 occur at 350-400Å compared to 550Å to 600Å for typical BARCs. The second reflectivity minimum at the same time occurs at 900 to 1000Å compared to a typical thickness of 1300 to 1400Å. Figure 14 shows a similar reduction in the required BARC thickness with DUV64 and DUV74 for achieving good reflectivity control over oxide on poly silicon as compared with DUV30 and DUV42.

4.2.4 Resist compatibility
Figures 15 and 16 show isolated and dense lines using Sumitomo's photoresist PEK120A-4 over DUV64. Work is still in progress to achieve good compatibility with ESCAP type DUV resists.

4.3 EXP99060 and ARC25 as 193nm BARC
4.3.1 Chemistries
There are two 193nm projects currently under development at Brewer Science. One is targeted for application at its second reflectance minimum thickness, while the other is targeted for use at its first minimum thickness. ARC25-8 was designed for the former, and it is already a commercialized product. EXP99060, as a first
minimum thickness BARC product, is in the optimization stage of production. Figure 17 represents polymer structure of ARC25.

4.3.2: Basic properties:
Table 4 lists some basic properties of ARC25 and EXP99060, respectively.

Table 4: Basic Properties of ARC25 and EXP99060

<table>
<thead>
<tr>
<th></th>
<th>MW</th>
<th>n</th>
<th>k</th>
<th>Etch rate*</th>
<th>First min.</th>
<th>2nd min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARC25</td>
<td>60,000</td>
<td>1.82</td>
<td>0.46</td>
<td>1.25</td>
<td>270</td>
<td>770</td>
</tr>
<tr>
<td>EXP99060</td>
<td>50,000</td>
<td>1.72</td>
<td>0.57</td>
<td>1.20</td>
<td>320</td>
<td>880</td>
</tr>
</tbody>
</table>

* HBr/O2, Selectivity to PAR710 photoresist

Figures 18 and 19 illustrate the reflectivity curve of ARC25 and EXP99060.

As shown in these figures, ARC25 can be used at both its first and second minima film thickness, and EXP99060 can be best used at its first minima film thickness.

The lithographic performance of ARC25 with PAR710 at 100nm resolution and EXP99060 with PAR710 at 110nm is shown in Figures 20 and 21.
5. Conclusions
Resolving the reflectivity control problem is a key challenge for advanced photolithography. Development of improved organic BARCs will require the identification of materials with superior optical properties, as well as acceptable etch and integration properties. Addressing other integration concerns such as defects, conformality, removal and dielectric integrity will also provide a complete process solution with excellent reflectivity control. Based on our technology, a series of new BARC materials has been developed to meet the semiconductor industry's standard for next generation lithography. We will continue working on the improvement of existing products, as well as new BARC materials for the leading edge lithography. New research projects such as BARCs for low k dielectric/resist poisoning, 193 dual damascene and 157nm applications are currently under development.

6. Acknowledgements
A portion of the work was supported by BMDO per contract DASG60-00-C-0044. The authors would like to thank Jim Lamb of Brewer Science Inc., for his technical guidance, as well as the support from Brewer’s Research, Engineering, and Applications members.

7. References
[7] PROLITH is a registered trademark of Finle Technologies.