A New Method to Characterize Conformality of BARC Coatings

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Abstract

In the semiconductor manufacturing industry, a bottom anti-reflective coating (BARC) is used to minimize thin film interference effects by reducing reflected light. As substrate topography becomes more complex with efforts to design more complex circuits, the effect of reflected radiation becomes more critical. The degree of conformality of the BARC coating plays an important role in lithography performance, which in turn affects the design of plasma etching processes. In this study, we propose a new method to measure the BARC coating conformality. The relationship between film thickness and horizontal distance from the step can be described by an exponential function. We found this profile is related to the properties of the coating material, such as molecular weight, the composition of formulation, the polymer structure, Tg of the polymer, thermal flow capability, and the crosslinking reaction, but is independent of step height, step width, and BARC thickness. The pitch affects the shape of the coating profile only when the spacing of features is smaller than a threshold that is related to coating material properties. The curvature of the profile indicates the uniformity of BARC thickness across the topography, which is a very good parameter to quantitatively describe the conformality of BARC coatings. Studies on Brewer Science BARC products confirm that the proposed conformality measuring method is in excellent agreement with observations. This method offers the option to separately consider the effects of coating processing, topography type, film thickness, and inherent material properties. It affords the predictability of BARC behavior for coatings that cover different topographies.

Keywords: bottom anti-reflective coating, BARC, conformal, planarizing, conformality

1. Introduction

In the semiconductor manufacturing industry, a bottom anti-reflective coating (BARC) is used to minimize thin film interference effects by reducing reflected light. As feature size becomes smaller and substrate topography becomes more complex with efforts to design more functional circuits, controlling the variation in critical dimension (CD) caused by the reflection of light from highly reflective substrates, interference of multiple layers of thin films, and photoresist depth of focus (DOF) is more critical. Decreasing the exposure wavelength or increasing the numerical aperture of the lens to improve resolution will lead to a decrease in DOF, and planarization of substrate topography may become necessary as optical lithography is pushed toward its resolution limits [1]. A planarizing coating produces a global flat surface and minimizes concerns related to photoresist DOF, but the difference in BARC thickness will cause a difference in reflectivity and a plasma etching bias when etching the BARC layer. On the other hand, as the exposure wavelength of the lithography scanner or stepper is decreased, there is an increase in reflected light from the underlying films [2]. Uniformity of BARC thickness is an important factor in finely controlling reflectivity. A few nanometers of variation in BARC thickness could cause a significant increase in reflectivity as a result of resist CD variation. A conformal coating produces uniform thickness on topography. Reflectivity control is improved and plasma etch bias is no longer an issue, but the resist must have enough DOF to compensate for the difference of resist height. Manufacturers usually have requirements for BARC conformality or degree of planarization corresponding to the substrate and processing method used. Although other process methods can form completely conformal or planarizing organic BARCs such as a highly conformal CVD BARC [3] or a contact planarization BARC [4], spin coating is still the most popular and the simplest method to apply a BARC layer.

A spin-on organic BARC is in general neither totally conformal nor completely planarizing. During the spin coating process, a polymer solution is deposited onto a wafer, and the wafer is rotated and accelerated up to its final rotation speed. Material is expulsed from wafer surface by the rotation motion, followed by the fluid thins, and the volatile solvent evaporates [5]. Four major forces act on a film during the spin coating process: centrifugal, capillary, gravitational, and viscous forces. The balance between centrifugal and viscous forces tends to produce an uniform film over the substrate, while capillary and gravitational forces result a flat or planar coating [1]. Planarization occurs locally due to the solvent concentration gradient that exists in thicker films. The solvent concentration gradient between the top and bottom of features caused by the thicker film dries slowly planarizes the local microscopically substrate by making

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volatile solvents diffuse up, and novolatile solids diffuse down from the vicinity region [6]. The relationships between evaporation rate of the solvent during spin coating and coating defects [7] and degree of planarization [1,6] have been studied and modeled. Polymer properties, such as molecular weight, have significant effects on the conformality of the coating film on vertical and sloping step topography. High molecular weight polymers usually form conformal coatings [8], and formulations that contain low molecular weight resins, low Tg resins, and plasticizer compounds form planarizing coatings [9].

Traditionally, the conformality or degree of planarization of a BARC is calculated by a simple equation that includes terms for the maximum top thickness, the minimum bottom thickness, and the step height as related to coating over topography [1,2,6,8,9]. Though this single point method gives a rough estimation of the conformality, it cannot represent the whole coating coverage and does not take into account the effects of material properties. This method is very sensitive to step size, step pitch, and BARC thickness [8]. A better method to describe the true conformality is greatly needed.

2. Experiment

2.1 Polymer synthesis

Polymers were synthesized by a radical polymerization, and a chain transfer agent was added to control the molecular weight. Chromophores were either on the polymer main chains or grafted on the side chains to ensure that the BARCs have enough absorbance at certain wavelengths. Molecular weight was measured by gel permeation chromatography (GPC).

2.2 Formulation

The BARC formulation was prepared by blending appropriate amounts and types of polymer, crosslinking agent, and catalyst. To make the solvent component of this BARC formulation, a mixture of propylene glycol methyl ether (PGME), propylene glycol methyl ether acetate (PGMEA), and ethyl lactate (EL) was used. These solvents are safe solvents that are acceptable for use in the semiconductor industry. The final solution underwent ion exchange to reduce metal ion content and was filtered through a 0.1 μm filter.

2.3 Thickness determination

BARCs were spin coated onto 4-inch wafers at a spin speed of 1500 rpm or 2500 rpm for 60 seconds to form the films, and then baked on a hot plate at 205°C for 60 seconds to let the films fully crosslink. A Gaertner ellipsometer was used to determine the film thickness. The solid concentration of each BARC formulation is controlled so that the film thickness is in the same range when it was coated on a flat wafer using the same spin speed.

2.4 Topography wafer

The features on the topography wafers were steps and trenches with right-angle corners. Three kinds of wafers were used, which had step heights of 700 nm, 500 nm, and 200 nm. Each wafer contained steps having different widths, specifically, 0.25 µm, 0.35 µm, 0.50 µm, 1.00 µm, 3.00 µm, and different pitches, from 1/1 dense lines to isolated lines and open areas.

2.5 Image analysis

SEM cross-section images were taken and analyzed by NIH *Image* 1.62 software. To find the boundary of the images, enhancement techniques were used to sharpen the edge of a profile. The data were transferred to Excel and fitted by a mathematical function.

3. Results and Discussion

3.1 Single point measurement

The conventional concept of a conformal BARC is one where the BARC layer has constant thickness across the topography. A planarizing BARC provides a coating layer that creates a planar surface. The commonly used definition of conformality in the semiconductor industry is a simple equation that is shown below, where T_1 is the maximum film thickness on the top of the step, T_2 is the minimum film thickness at the bottom of the trench, and T_0 is the step height. Figure 1 shows the diagram of measurements on dense and isolated features.

$$\boxed{\text{Conformality} = 1 - \frac{T_2 - T_1}{T_0} \times 100\%}$$

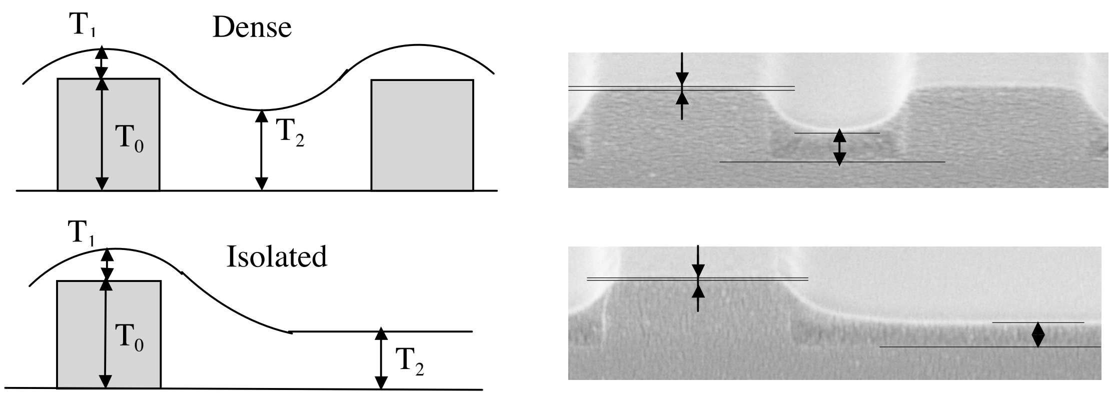


Figure 1. The single point measurement and conformality calculation.

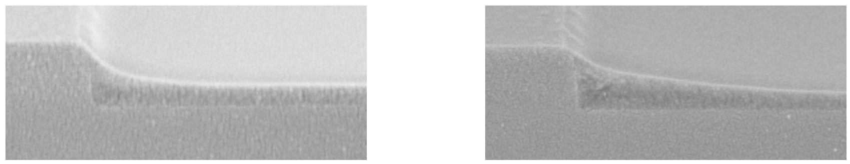
This definition has some weaknesses. One is the thickness at the top of the step or at the bottom of the trench is not a constant, which means T_1 and T_2 do not capture all the information of the coating thickness. Moreover, when the feature size is small and the BARC thickness is thin (a typical BARC thickness is 30 nm to 100 nm), it is difficult to measure such short distances from an image due to the resolution limitations of the SEM. Also, previous work [6,8] has indicated that this method is sensitive to topography and BARC thickness: smaller features, denser features, and thicker films are less conformal.

In order to compare material fairly and eliminate the effects of topography and film thickness, we retained the same test conditions. Four Brewer Science commercial BARCs were tested under the following conditions: 60 nm film thickness on a flat wafer and the topography wafer that consists of square-shaped step with 200 nm step height, 500 nm step width, S/L=1/1 dense pitch, and S/L=5/1 isolated pitch. Table 1 shows the conformality calculation results from T_1, T_2, and T_0 measurements on dense and isolated features. The data do not show any difference among the four samples. The only trend we can see here is that conformality in a dense area is lower than that in an isolated area.

Table 1. Calculation using the equation $\text{Conformality} = 1 - \frac{(T_2 - T_1)}{T_0} \times 100\%$.

Sample Name	Type	Conformality Dense	Conformality Isolated
DUV30J-6	Planarizing	66%	73%
DUV42P-6	Conformal	63%	72%
DUV52D-6	Planarizing	64%	82%
DUV112-6	Planarizing	61%	78%

In Figure 2, the enlarged SEM images of DUV42P-6 and DUV112-6 on the corner of an isolated step clearly show the differences in profile. DUV42P-6 is a conformal BARC because it has a more uniform thickness and good corner coverage, while, the thickness of DUV112-6 gradually changes from the step to the open area, and more material accumulates at the bottom, which is a typical planarizing BARC. In the case of DUV112-6, the minimum thickness at the bottom, T_2, does not show the relatively large mass of material near the corner of the step. As a result, DUV112-6 has a thinner bottom layer and a higher conformality number than DUV42P-6 has in Table 1, which is not consistent with the SEM images.



a. DUV42P-6 b. DUV112-6

Figure 2. The SEM cross-section images enlarged at an isolated step corner.

A better method to characterize conformality needs to be developed which will reflect the coating profile over all topography and is related only to material properties.

3.2 New method to characterize conformlaity

3.2.1 Description of new method

Single point measurement cannot describe the entire coating layer. As Figure 3 shows, the coating thickness is not a constant but a function of position in a horizontal direction. A conformal BARC has a long flat tail and rapid transition range at the edge of the step, whereas a planarizing BARC has more material accumulated at the step corner and the thickness continually changes over a long range. At the corner of an isolated step, where material can flow freely since no nearby features impede material movement, the shape of the coating is only related to the properties of the material and its surface interaction with the substrate. The coating profile across the topography shows the biggest difference at an isolated step. Therefore this feature was chosen for conformality characterization. The profile near an isolated step is taken from the SEM image by the NIH *Image* 1.62 software. Some optional enhancements were applied on images to sharpen the edge. Figure 4 is an example that shows how to find the coating edge and transfer an image to a data file.

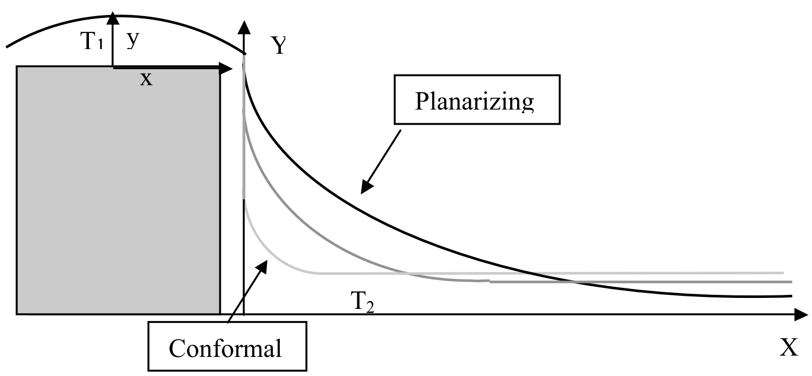
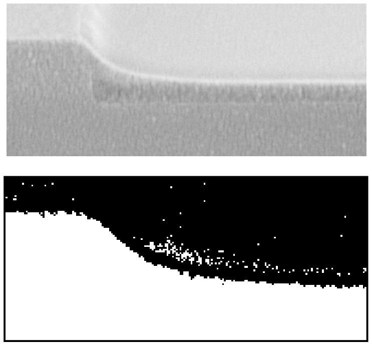


Figure 3. The diagram of conformal and planarizing coatings.



0	139
7	136
15	132
20	129
27	124
35	117
40	114
47	109
55	102
62	94
72	87
79	82
87	74
92	72
99	67
109	62
117	57
129	50
139	45
149	42
161	37
169	35
179	30
196	27
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246	17
261	15
280	15
305	12
323	10
347	7
367	7
390	5
404	5

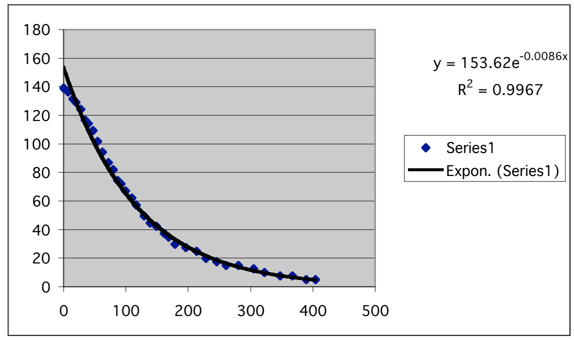


Figure 4. Finding the coating edge and transferring the image file to a data file.

The data are well fitted by the exponential function $y = ae^{\pm bx}$, where y is the total thickness less the thickness of the open area, and x is the distance from the step. In this equation, b represents the curvature of the line, which indicates how conformal the coating layer is. + or – comes from left or right side of the step. a is the height at the top corner of the step, which shows the corner coverage. The curve here does not fit the exponential function well because the coating followed the shape of the step and turned to other direction. Figure 5 shows the profile curves at an isolated step of the BARC samples that were discussed in 3.1. Table 2 lists the b values of the exponential function. From Table 2, we can see DUV42P-6 has the highest value for b, which means it is much more conformal than the other BARCs. DUV52D-6 is the most planarizing BARC of the four because it has the lowest value for b.

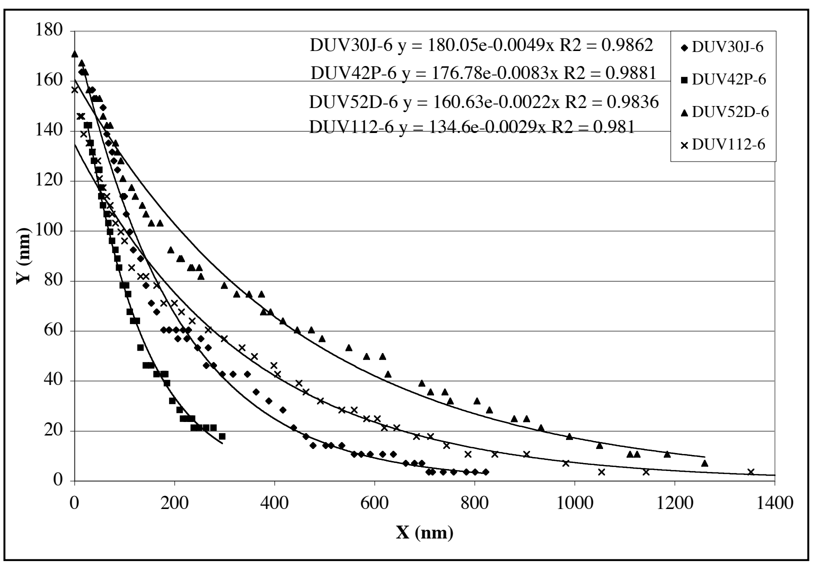


Figure 5. Coating profiles taken from SEM images and exponential function lines (for an isolated step 200 nm high and 500 nm wide.)

Table 2. b values of exponential function fitting lines from Figure 5.

Sample name	Type	Conformality b ($\times 10^{-4}$)
DUV30J-6	Planarizing	49
DUV42P-6	Conformal	83
DUV52D-6	Planarizing	22
DUV112-6	Planarizing	29

3.2.2. Evaluation of Brewer Science BARCs

Many Brewer Science products have been evaluated by the new method. The results are shown in Figure 6 and are separated into four groups: i-line (light gray shading), KrF (hatch-marked), ArF second minimum (dark gray), and ArF first minimum (black). i-CON, as its name suggests, is a conformal i-line BARC that exhibits very high conformality. In the KrF group, DUV42, DUV44, and DUV74 are conformal BARCs, and DUV30, DUV52, DUV112, and DUV114 are planarizing BARCs. DUV74 shows the highest conformality because of its unique chemistry and crosslinking mechanism. The most planarizing KrF BARC is DUV52, which has very good via fill performance for dual damascene application. In the ArF second minimum group, ARC25 is the most conformal BARC, ARC81 is the most planarizing BARC with a very good via fill property. As a first minimum BARC, the basic requirement is high conformality because a thin layer of BARC must cover the topography. ARC27, ARC28, and ARC33 are able to provide uniform coverage across the topography because of their high conformality.

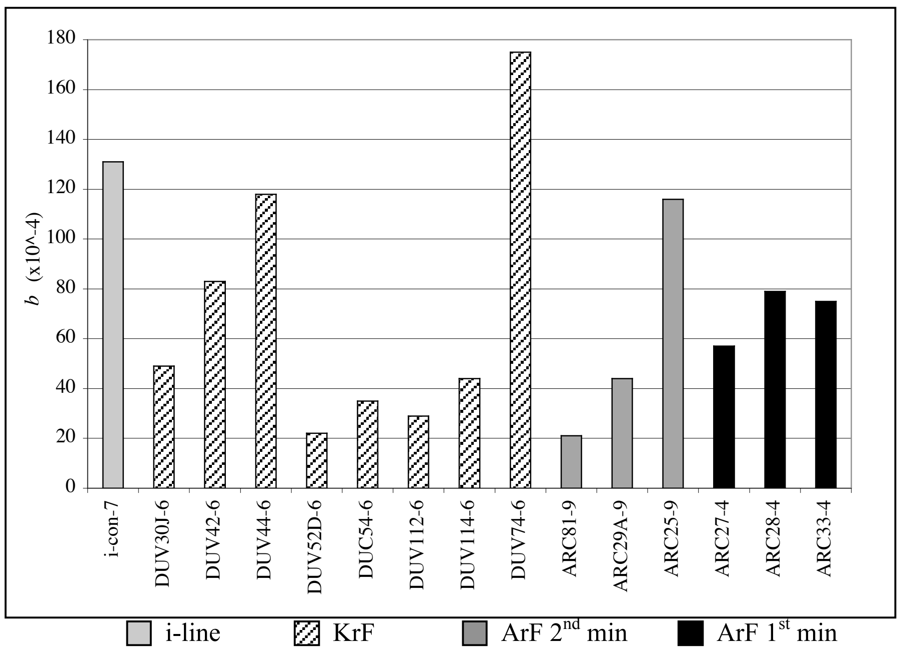


Figure 6. Conformality of Brewer Science BARC products.

Comformality is related to material properties such as molecular weight, polymer Tg, chemical structure, solvent system, and additives in the formulation. Table 3 shows that high molecular weight and high Tg polymers form highly conformal coatings.

Table 3. Conformality related to polymer properties.

Sample	Molecular weight	Polymer Tg (°C)	Conformality b ($\times10^{-4}$)
DUV42P-6	High	78	83
DUV112-6	Low	32	29
DUV52D-6	Low	32	22
ARC29A-9	High	72	43
ARC81-9	Low	0	22

3.2.3. Step width effect

In this experiment, we kept the parameters the same except for the step widths (0.3 μm, 0.50 μm, and 3.0 μm) to see how the conformality (b value of the new method) changes. From Figure 7, we see a general trend that the conformality over a narrow step is slightly higher than that over a wide step, but the difference between the steps is small when the same material is applied on. Larger differences were found among different materials. The results indicate that conformality is more sensitive to material properties and less sensitive to step width, which is in agreement with our prediction.

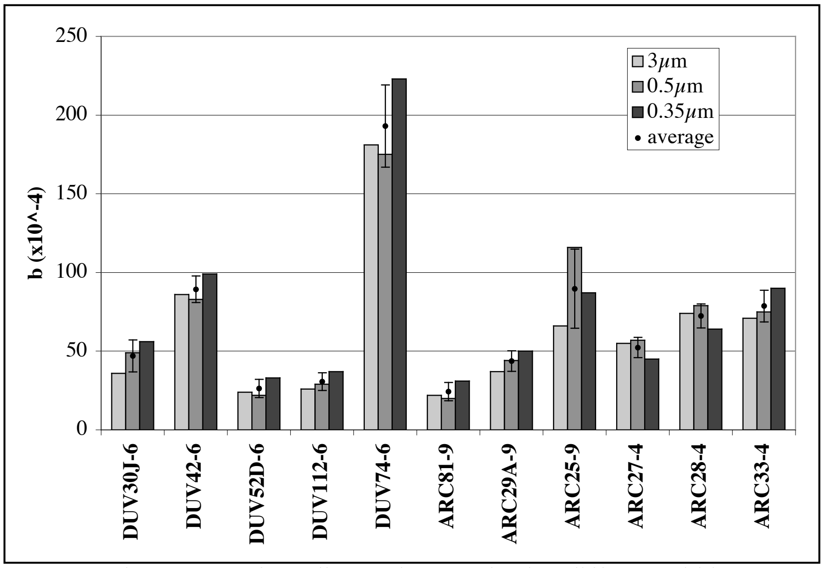


Figure 7. Conformality on the steps having different widths.

3.2.4. Step height effect

In this experiment, we kept the parameters constant except for the step heights (200 nm, 500 nm, and 700 nm). Two Brewer Science BARCs (ARC81-9 and ARC29A-9) were coated onto the patterned wafers, and the measured results are listed in Table 4. The conformality at different step heights is constant: b of ARC81-9 is about 30×10^{-4}, and b of ARC29A-9 is about 60×10^{-4}. When the step heights are 200 nm and 500 nm, the coating profile at both sides of the step is almost the same. But on a 700-nm step, the coating profiles located on either side of the step are different. Figure 8 shows ARC29A-9 coated on a 700-nm step. One side faces toward the center of the wafer, and the other side faces toward the edge of the wafer. Table 4 lists the two conformality numbers from the two sides of the step. Because the step is too high compared with the very thin layer of coating, the step actually acts as a wall that blocks material flow.

Table 4. The conformality on the steps with different step heights.

Step height (nm)	ARC81-9 b ($\times10^{-4}$)	ARC29A-9 b ($\times10^{-4}$)
200	30	59
500	32	60
700	30 40	42 59

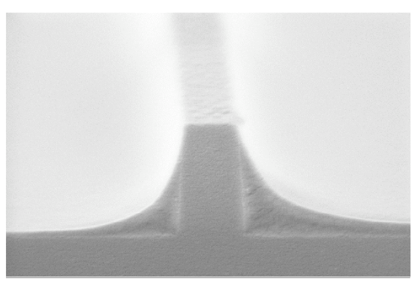


Figure 8. ARC29A-9 coated on a step that is 700 nm high and 500 nm wide.

3.2.5. Step pitch effect

At an isolated step, the coating thickness changes gradually from the step edge to some distance away from the step, where the thickness becomes uniform in the open area (Figure 9). The thickness is considered a constant when the thickness variation is less than one pixel in the image files and not measurable from SEM images. In Figure 9, we define the distance from the edge of the step to the point where the thickness becomes a constant as the threshold length L. Conformal BARCs have shorter threshold lengths than those of planarizing BARCs. Table 5 lists some examples.

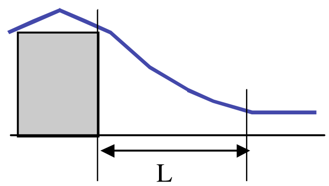


Figure 9. The definition of threshold length L.

Table 5. Threshold length L of different types BARCs.

Samples	Type	Threshold length L (nm)	Conformality b ($\times 10^{-4}$)
DUV52D-6	Planarizing	1200	22
DUV42P-6	Conformal	300	83
ARC81-9	Planarizing	1400	22
ARC29A-9	Conformal	700	43

At an isolated step, material can flow freely from the vicinity of the step to the flat area of the wafer. The shape of the coating profile is only related to material viscosity, solvent evaporation rate, surface tension of coating fluid, and the type of substrate. However, if the material flow is interrupted by another feature such as a second step, predicting the coating profile becomes more complicated as both material properties and step pitch must be taken into account.

If the space between two steps is larger than twice the threshold length L, the conformality is the same as that for an isolated step because there is no interaction between nearby steps. When the space between two steps is smaller than twice the threshold length L, the conformality and minimum film thickness at the bottom begin to change with the pitch. Figure 10 shows conformality b and the bottom thickness changing with pitch, where each BARC has three experimental points, indicated as solid points, and one threshold pitch calculated from threshold distance, indicated as hollow points. We assume the conformality and the bottom thickness at the threshold pitch are the same as those at an isolated pitch. Once the pitch becomes smaller than the threshold pitch, the conformality and the bottom thickness increase linearly as line/space pitch increases.

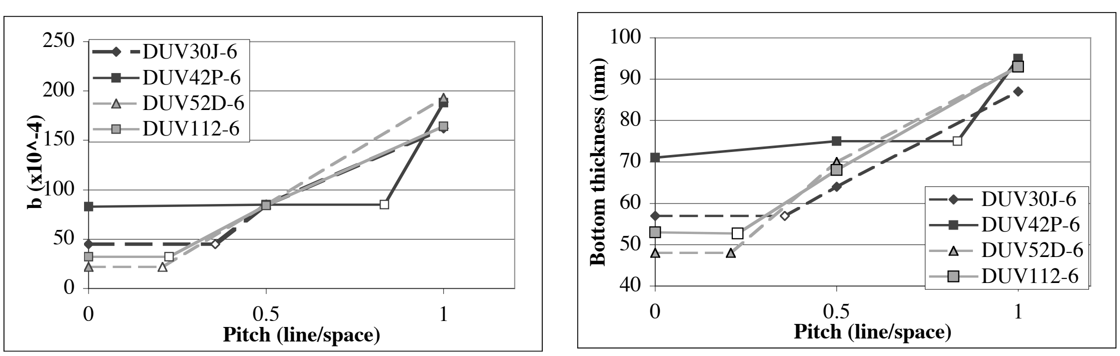
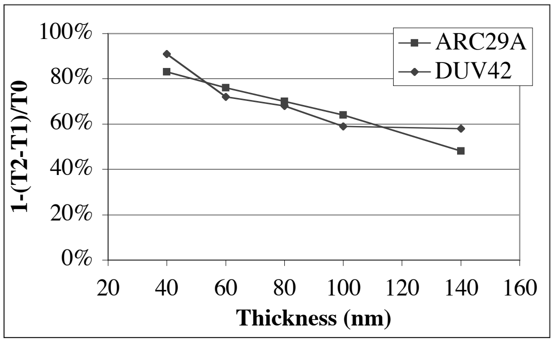


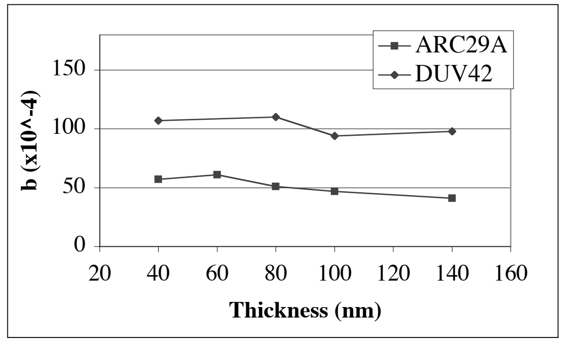
Figure 10. The conformality b and the bottom thickness changing with pitch, where the solid points are experimental data, and the hollow points are threshold points calculated from threshold distance.

3.2.6. Film thickness effect

It is difficult to compare conformality of the coatings having different thicknesses using a single measurement method because the conformality result changes as thickness varies, as shown in Figure 11a. However, the new method shown in Figure 11b gives a constant result at any thickness. For both methods, the conformality decreases slightly as the coating thickness increases, but in the new method, the effect of material properties is much larger than the effect of the film thickness. For two BARCs with significantly different thicknesses, we can still distinguish which one is more conformal.



a. Single point method



b. New method

Figure 11. Thickness effect on conformality.

4. Conclusion

Conformality is an important thin film property for BARC applications in the semiconductor industry. The old method calculated from single point measurement cannot sufficiently describe entire coating behavior and is sensitive to topography and processing. The new method we proposed in this paper is related only to material properties and describes BARC coating behavior across topography. Studies on Brewer Science BARC products confirm that the proposed conformality measuring method is in excellent agreement with observations. The new comformalty characterization is related to the properties of the coating material, such as molecular weight, the composition of formulation, the polymer structure, Tg of the polymer, and the crosslinking reaction, but is independent of step height, step width, and BARC thickness. The conformality on the different pitches can be predicted. The new method offers the option to separately consider the effects of coating processing, topography type, film thickness, and inherent materials properties. The coating behavior of BARCs over different topographies may be predicted.

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