Via fill properties of organic BARCs in Dual Damascene application

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ABSTRACT

With the introduction of copper as the interconnect metal, the Dual Damascene (DD) process has been integrated into integrated circuit (IC) device fabrication. The DD process utilizes organic bottom anti-reflective coatings (BARCs) not only to eliminate the thin film interference effects but also to act as via fill materials. However, three serious processing problems are encountered with organic BARCs. One is the formation of voids, which are trapped gas bubbles (evaporating solvent, byproduct of the curing reaction and air) inside the vias. Another problem is non-uniform BARC layer thickness in different via pitch areas. The third problem is the formation of fences during plasma etch. Fences are formed from materials that are removed by plasma and subsequently deposited on the sidewall surrounding the via openings during the etching process.

Voids can cause variations in BARC top thickness, optical properties, via fill percentage, and plasma etch rate. This study focuses on the factors that influence the formation of voids and addresses the ways to eliminate them by optimizing the compositions of formulations and the processing conditions. Effects of molecular weight of the polymer, nature of the crosslinker, additives, and bake temperature were examined. The molecular weight of the polymer is one of the important factors that needs to be controlled carefully. Polymers with high molecular weights tend to trap voids inside the vias. Low molecular weight polymers have low Tg and low viscosity, which enables good thermal flow so that the BARC can fill vias easily without voids. Several kinds of crosslinkers were investigated in this study. When used with the same polymer system, formulations with different crosslinkers show varying results that affect planar fill, sidewall coverage, and, in some cases, voids. Additives also can change via fill behavior dramatically, and choosing the right additive will improve the via fill property. Processing conditions such as bake temperature also greatly affect via fill. Depending on the polymer thermal property and crosslinking reaction, varying the bake temperature can change the via fill behavior of the BARC.

By understanding the nature of the polymer, the crosslinking reaction, and the processing conditions, we are able to design BARCs with better flow property to provide planar topography without voids inside the vias.

Keywords: BARC, Dual Damascene, voids, via fill, flow property

1. INTRODUCTION

As critical dimensions in IC design continue to shrink to less than 250 nm, copper has been introduced as the metal to replace aluminum for inter-level wires and inter-connects. Copper has many advantages over aluminum, such as low resistance when deposited in narrow trenches and low power capacitance, which can reduce the size and cost. [1] Because copper is difficult to etch, the DD process has been applied to IC device fabrication. During the DD process, the contact and via hole are typically etched before the trench etching. The step of trench etching requires planarizing surface topography of high aspect vias in order to reduce lithographic bias, allow more focus margin during the wafer exposure, and control the final CD. An organic BARC works in this process not only to eliminate pattern degradation and line width variation in the patterning trench layer, but also to provide the fill material that covers the topography surface of dielectric layer. [2]

Organic BARC materials have been developed for DD application. Designing DD BARCs is a challenge because they must achieve good via and trench fill, planarize the top surface, be compatible with photoresists, and withstand dielectric layer plasma etching. Three serious processing problems are encountered with organic BARCs. One is the formation of voids, which are trapped gas bubbles inside the vias. The gas could be a solvent vapor, a by-product of the curing reaction, or an air bubble sealed during polymer thermal flowing. Voids can cause non-uniform etch rates, which will leave some vias insufficiently protected by the BARC during the trench etching. Another processing problem is that the

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thickness of the BARC layer is non-uniform in different via pitch areas. Because a dense area needs more material to fill more vias, the thickness over a dense area will be thinner than the thickness over an isolated area, which makes resist thickness variation significant, and produces subsequent differences in trench width. [3,4] Yet another processing problem is the formation of fences during plasma etch. Materials are removed by the plasma and subsequently deposited on the sidewall surrounding via openings during the etching process. The altered BARC-sidewall material may not be removable by the same resist stripping step. [4]

This study focused on the factors that influence the formation of voids. Properties of polymer, reactivity and efficiency of crosslinker, the function of additives and processing conditions have different distribution on voids controlling. By understanding each factor, we are able to design BARC for DD application.

2. EXPERIMENT

Base polymers were made in a 3-neck glass flask. A chain transfer agent was added to control molecular weight. A chromophore that has high absorption at 248 nm or 193 nm was chemically grafted onto the polymer later in the same reaction set. The BARC formulations consisted of a polymer grafted with a chromophore, a crosslinker, a catalyst of acid or a thermal acid generator, and organic solvents. Ion exchange beads were used to remove ions. All formulations were filtered through 0.1 µm filters.

Eight-inch via wafers used in this study (made at IMEC) contain a 1 µm thick layer of silicon dioxide on the top. Vias are 1 µm deep through the silicon dioxide layer. The diameters of the vias were 0.25 µm and 0. 2 µm, and aspect ratios were 4 to 5. Via holes were patterned at various pitches (dense, semi-dense, and isolated) with hole-to-space ratios at 1:1, 1:1. 5, and 1:5. Wafers were cut into small chips, and each chip contained at least 9 dyes. BARC samples were manually dispensed on a chip, spin coated at 1500 rpm for 60 seconds, and then baked on a hot plate at a temperature between 130°C and 225°C to form a crosslinked film that is resistant to solvents and compatible with resists. The top surface coverage and via fill profile were evaluated by examining SEM cross-sections images.

Molecular weight was determined by gel permeation chromatography (GPC). Polymer thermal properties were tested on a DSC 2920 (TA Instruments Inc.) under the conditions of modulated ±0.5°C every 60 seconds with temperature ramping of 3°C/min. Rheology was carried out on an AR2000 rheometer (TA Instruments Inc.). Rheology of the BARC formulations showed flow properties and crosslinking reaction. The viscosity was very low before crosslinking and solvent evaporation, but it increased rapidly once the polymer chains were crosslinking. The samples were loaded between two parallel plates. Viscosity data were recorded with temperature ramping under certain torque, oscillation stress, and frequency conditions.

3. RESULTS AND DISCUSSION

3.1 Effect of polymer molecular weight and glass transition temperature

During this study, four absorptive polymers that have the same chemical structure but different molecular weights were synthesized. All polymers were formulated with the same crosslinker, catalyst, and solvents. The ratios were the same for the four formulations. Table 1 shows the molecular weights and glass transition temperatures (Tg) of the polymers. Figure 1 is the plot of Tg versus molecular weight. Polymer Tg increases as molecular weight increases. Figure 2 shows SEM cross-section images of the via fill qualities of the four polymers. The polymer with the lowest molecular weight filled vias well. The others all have voids. The polymer with the highest molecular weight exhibits the worst via fill properties.

Table 1. Molecular weight and Tg of polymers

Polymer	**GPC Mw**	**Tg** (°C)
Polymer 1	8×10^3	35
Polymer 2	11×10^3	53
Polymer 3	16×10^3	62
Polymer 4	54×10^3	78

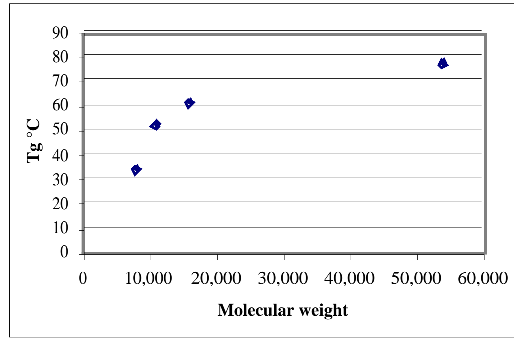
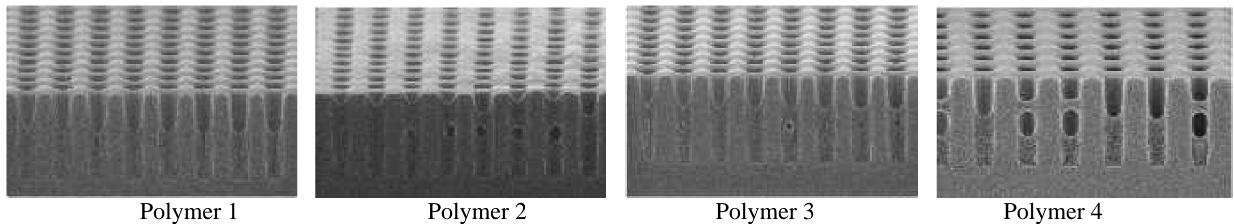


Figure 1. Tg increases as molecular weight increases.

The voids were formed when wafers were baked at high temperature on a hot plate. During baking, the polymer on the top surface flows down to the bottom of vias, but the polymer becomes immobile as soon as crosslinking reaction takes place. The time during which the polymer can flow is very short. The polymer rheology is one of the key factors that affect via fill properties. Assuming the speed of the crosslinking reaction for the four polymers is the same because they have same chemical structure and same formulation, the polymer having the lowest Tg has the lowest melting viscosity, which facilitates good thermal flow. The melting viscosity of the polymer with the highest Tg is high, which trends to sealed a bubble easily in each via when the viscous polymer flows slowly and connects at the neck range of vias. In Figure 1, the Tg of Polymer 1 is much lower than others and the polymer chains have less entanglement, which enables Polymer 1 to move into the vias smoothly.

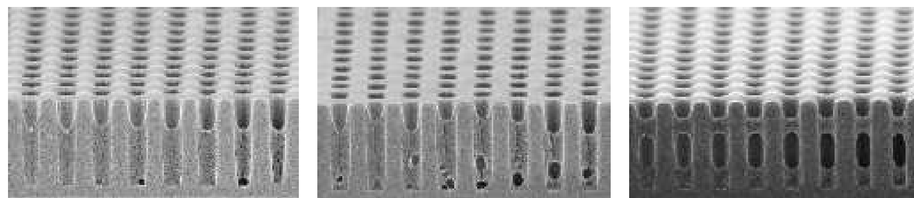


Polymer 1 Polymer 2 Polymer 3 Polymer 4

Figure 2. SEM cross-section images of via fill properties of four polymers with different molecular weights

3.2 Effect of crosslinker

The reactivity and efficiency of the crosslinker have a significant effect on via fill performance because the speed of crosslinking reaction is another key factor to control polymer thermal flow time and capability. Three crosslinkers have been studied. All formulations were made using the same polymer, catalyst, and formulator but with different crosslinkers. Figure 3 shows the SEM images of these formulations with different crosslinkers.



Crosslinker 1 formulation Crosslinker 2 formulation Crosslinker 3 formulation

Figure 3. The SEM images of the formulations with different crosslinkers

Three formulations show different via fill behavior. The crosslinker 1 formulation has little voids at bottom, which are caused by surface dewetting. Otherwise, the crosslinker 1 formulation filled the vias well. The crosslinker 2 formulation produced many small voids of varying sizes. The crosslinker 3 formulation trapped one big void in each via.

To study the reactivity of the three crosslinkers, the formulations were tessted on a rheometer. The crosslinking temperature was defined by the threshold of viscosity curve. Table 2 shows the crosslinking temperatures of the three formulations. The reaction speed of crosslinker 3 is almost twice as fast as that for crosslinkers 1 and 2. The crosslinking temperature of the crosslinker 3 formulation is much lower than that of the others. The polymer has no time to flow down to the bottom of vias; instead, the polymer is frozen at the necks of the vias, and one large void is trapped in each via. The crosslinking temperature of the crosslinker 2 formulation is a little lower than that of the crosslinker 1 formulation, but crosslinker 2 reacts more efficiently and forms a high crosslinking density network. Polymer shrinkage and volatile compounds, such as solvent vapor and the small molecular weight compounds produced during the crosslinking reaction, generate many voids. The crosslinking temperature of the crosslinker 1 formulation is high and its crosslinking density is low, which makes it the best choice for a via fill BARC.

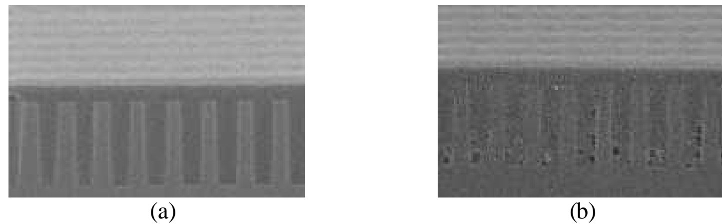
Table 2. Crosslinking temperature measured on rheometer

Formulation with crosslinker	Crosslinking temperature (°C)
Crosslinker 1	144
Crosslinker 2	132
Crosslinker 3	89

3.3 Effect of additives

Via fill properties are very sensitive to polymer thermal flow and crosslinking reaction. Adding additives into formulations can change the polymer flow and reaction properties, which can improve via fill dramatically. Two examples are discussed in this paper.

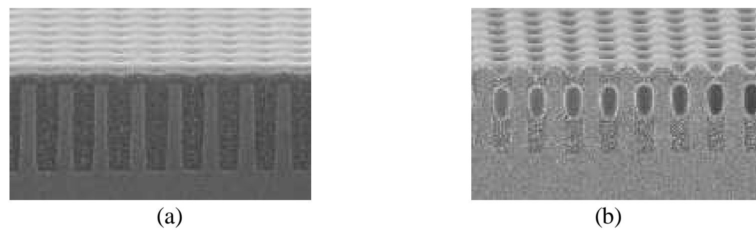
DUV52® is a commercial product from Brewer Science, Inc., which is a 248 nm BARC with very good via fill properties. The DUV52 formulation contains additives. If these additives are removed from formulation, voids appear. In Figure 4, the image on the left shows DUV52, and the other is the formulation without additives. DUV52 exhibits very good via fill performance, but the formulation without additives in Figure 4 (b) produced voids. In this case, the additives reduced the crosslinking speed, which allowed the volatile compounds to evaporate without leaving voids.



(a) (b)

Figure 4. SEM cross-section image of DUV52 with (a) and without (b) additives

ARC33® is another commercial product from Brewer Science, Inc., which is a via fill BARC for 193 nm application. Formulation B, made from the ARC33 formulation without any additives, always showed voids [5]. Figure 5 shows the original ARC33 formulation on the left and formulation without additives on the right. In this case, the additives changed the polymer flow properties and therefore the polymer can flow into the bottom in a short time before the crosslinking reaction takes place.



(a) (b)

Figure 5. SEM cross-section images of ARC33 with (a) and without (b) additives

3.4 Effect of bake temperature

Baking is an important step to reshape the topography. During the baking process, the solvent evaporates, chemical reaction forms the crosslinked network, and the by-product from reaction evaporates. Also the polymer has the capability to reflow because its viscosity decreases. The bake temperature setting affects the chemical and physical properties of film, and, as a result, the polymer's via fill performance changes.

Figure 6 shows SEM cross-section images of two samples baked at 175°C and 225°C. Sample A exhibited good via fill baked at 175°C, but it showed voids baked at 225°C. In this case, the higher temperature increased crosslinking speed, and crosslinking density became high very quickly, volatile compounds could not easily escape from vias, and voids were produced in the vias. Sample B has voids at both 175°C and 225°C, but the voids become smaller when the bake temperature is 225°C. In this case, the higher temperature decreases the viscosity of the polymer, therefore the polymer can flow faster.

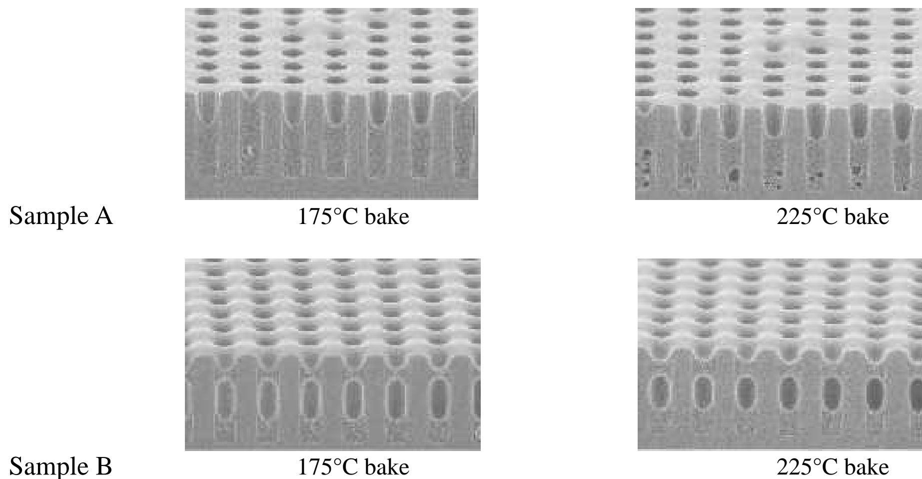
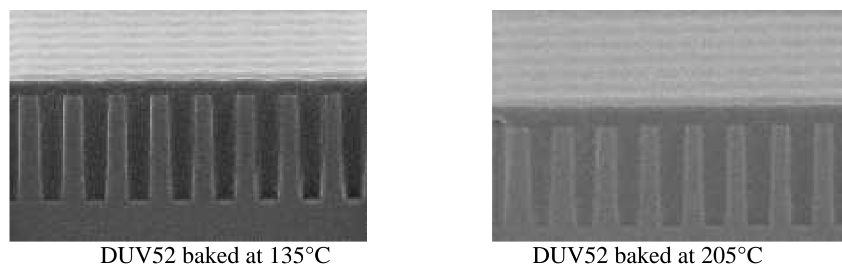


Figure 6. SEM cross-section images of two formulations baked at two temperatures

Depending on which parameters, polymer viscosity or crosslinking reaction, affects the via fill property mostly, different results can be observed. For the polymer that has a high melting viscosity, a high bake temperature will help to reduce viscosity and get better via fill. For the polymer that has a high crosslinking speed, a low bake temperature will slow down the crosslinking reaction, which gives volatile compounds time to get out of the vias.

DUV52 and ARC33 do not show any void formation problem baked at 130°C to 225°C. By carefully adjusting the types and ratios of polymer, crosslinker, catalyst, additives, and solvents, the formulations can satisfy the requirements for good via fill and good compatibility with the photoresist. The processing window could be very broad. Figure 7 shows SEM cross-section images of DUV52 baked at two different temperatures. They are all void free.



DUV52 baked at 135°C DUV52 baked at 205°C

Figure 7. SEM cross-section images of DUV52 baked at different temperatures

3.5 Design of new BARC

A new BARC for DD applications has been developed. This new polymer has very low molecular weight and its Tg is 0°C. Crosslinker 3 discussed in section 3.2 is used in this DD BARC formulation. The polymer has a unique chemical structure, and, from rheology data, its crosslinking reaction is much slower than other polymers. This BARC does not need additives because it is a polymer with very low molecular weight, low Tg, low melting viscosity, and low reactivity crosslinker. Figure 8 is an SEM cross-section image of the new BARC. This BARC exhibits very good planarization and via fill performance. Compared to the previous polymers, it has a more uniform fill, less sidewall coverage.

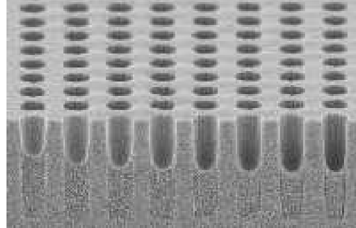
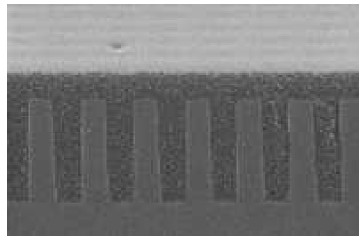
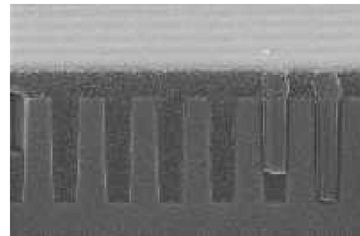


Figure 8. SEM cross-section image of new BARC

Also, the processing window is broad. Figure 9 shows no voids were appeared in vias baked from 135°C to 225°C. High baking temperature produced a high crosslinking density film, which can be seen from the right image in Figure 9. The material is pulled out of the vias during the preparation of SEM sample, which indicates the material is too hard to be broken. However, the high crosslinking network was formed slowly, which gave enough time to polymer thermal flow and volatile compounds evaporation.



New BARC baked at 135°C



New BARC baked at 225°C

Figure 9. SEM cross-section image of New BARC baked at tow different temperature

The advantage of this new BARC is not only good via fill performance, but also broad formulating and processing windows, which allow us to adjust the formulation and processing conditions to make the BARC compatible with the photoresists.

4. CONCLUSION

The two most important parameters that affect via fill properties are polymer rheology, such as Tg, melting viscosity, and thermal flow property, and crosslinking reaction, such as reaction speed and crosslinking density. To improve polymer rheology properties, we can choose the polymer with a low Tg and low molecular weight, add additives that can decrease melting viscosity, and bake wafers at a high temperature. To control the crosslinking reaction, we can use a low reactivity crosslinker, add additives that can reduce the speed of the crosslinking reaction, and bake the wafers at a lower temperature.

The challenge of creating a DD BARC is that the requirements of good via fill properties and compatibility with the photoresists have to be satisfied. If we understand the function of each component in the formulation and the behavior of polymer flow and crosslinking reaction, the formulating and processing windows can be found.

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REFERENCES

1. Peter Singer, "Tantalum, Copper and Damascene: The Future of Interconnects," *Semiconductor International*, June 1998.
2. James Lamb, Xie Shao, "Improved Fill Material for Dual Damascene Processes," U.S. Patent No. US 6,391,472 B1, May 21, 2002.
3. Owen Hehmeyer, Abhishek Singh, et al., "Bottom antireflective coatings: fluid property characterization and wetting tendency," *Proceedings of SPIE*, vol. 4690, 2002.
4. Stanley Wolf, *Silicon Processing for the VLSI Era*, Volume 4 - Deep-submicron process technology, chapter 15. Lattice Press, California, 2002.
5. Kelly A. Nowak, "Void elimination research in bottom antireflective coatings for Dual Damascene photolithography," *Proceedings of SPIE*, Vol. 5039, 2003, pp. 891-901.