

Study of Iso/Dense Bias of BARCs and Gap-Fill Materials on Via Wafers

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ABSTRACT

The topography of a back-end wafer contains high-aspect vias that are unevenly distributed on a wafer with pitches ranging from 1:1 dense to isolated. The difference in via density causes thickness bias across the wafer, which causes the shift of resist depth of focus and critical dimension swing. The bottom anti-reflective coating (BARC) topography is formed basically after spin coating and reshaped through thermal reflowing when the coating is baked at high temperature to cure the film. In this paper, we discuss the thicknesses at isolated and dense via patterned areas in the spin-coating process and the baking process.

Spin coating is a method commonly used to cast BARC and gap-fill materials on silicon wafers. The first stage of spin coating is the deposition of the coating liquid onto the wafer. The second stage is when the substrate is accelerated up to its final, desired rotation speed. The third stage is when the substrate is spinning at a constant rate and fluid viscous forces dominate the fluid thinning behavior. The fourth stage is when the substrate is spinning at a constant rate and solvent evaporation dominates the coating thinning behavior. Viscous flow and solvent evaporation occur throughout all stages. After spin coating, high-temperature baking cures the film and makes it insoluble in organic solvents that are used in the next spin-coating step. However, this step also gives the polymer a chance to undergo thermal flow because the bake temperature is much higher than the polymer's glass transition temperature (T_g). A chemical reaction occurs at the same time to form a polymer network that stops the thermal flow. The study of how far material can flow before the gel point of the polymer has been reached is presented in this paper.

The calculation of the material transformation due to solvent evaporation and polymer rheometry is based on dynamic and kinetic effects. The work described in this paper showed how the parameters related to material properties and to the chemical reaction of crosslinking affected iso/dense bias. This work gives us guidance regarding what kind of materials and process conditions are good for planarization.

Key words: dual damascene, BARC, gap-fill material, iso/dense bias

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. With the introduction of copper as the interconnect metal, the dual damascene (DD) process has been integrated into integrated circuit (IC) device fabrication. The damascene process is complex because there are a number of different integration possibilities. The via-first process, which is the most popular process, requires the incorporation of a BARC or gap-fill material into the scheme to planarize the surface before printing trenches. Because the distribution of the contact vias is uneven in one die, the film on the top of vias in a densely patterned area will be thinner than the film in an isolated via area. This thickness bias causes reflectivity control failure, non-uniform resist thickness, a shift of depth of focus, CD variation, and plasma etch bias.

Much research has been done in the past to seek material and processing solutions to reduce iso/dense bias. Using gap-fill material is one possible solution. In this approach, applying a thick layer of a gap-fill material to fill the deep vias and planarize topography is followed by plasma etching or chemical mechanical polishing (CMP) to remove the extra thickness. If the gap-fill material has no anti-reflective function, a thin BARC layer can be applied on top.¹ Brewer Science Inc., has planarizing BARCs (DUV52, ARC@81 and ARC@82) and gap fill materials (GF33, GF43, and GF52) that are designed for this application. Some gap-fill materials are developer soluble, so instead of plasma etch back, the thick material on the top of vias can be removed by a normal developer wash followed by dionized (DI) water

rinse. This process increases wafer throughput, reduces particles generated from wafer transfer and plasma etching.² Contact planarization developed by Brewer Science is the another convenient method to achieved a flat surface.³

However, using a single coating layer that does not require an additional processing step is still the first choice in industry because of the low cost and issues related to changes in tool design. In this paper, we discussed polymer solution flow, polymer thermal reflow, and chemical reaction during spin coating and hot plate bake. We also establish the relationship between material properties and bias, and look for the solution based on material's intrinsic properties.

2. THEORY

2.1. Spin coating

Organic BARCs and gap-fill materials that contain polymers, additives, and solvents are applied on wafers commonly by spin coating. The first stage of spin coating is the deposition of the coating liquid onto the wafer. The second stage is when the substrate is accelerated up to its final, desired rotation speed. The third stage is when the substrate is spinning at a constant rate and fluid viscous forces dominate fluid thinning behavior. The fourth stage is when the substrate is spinning at a constant rate and solvent evaporation dominates the coating thinning behavior. Viscous flow and evaporation occur throughout all times, however, at an engineering level, the viscous flow effects dominate early on while the evaporation processes dominate later. Figure 1 shows the details of material movement at the different stages of spin coating.⁴

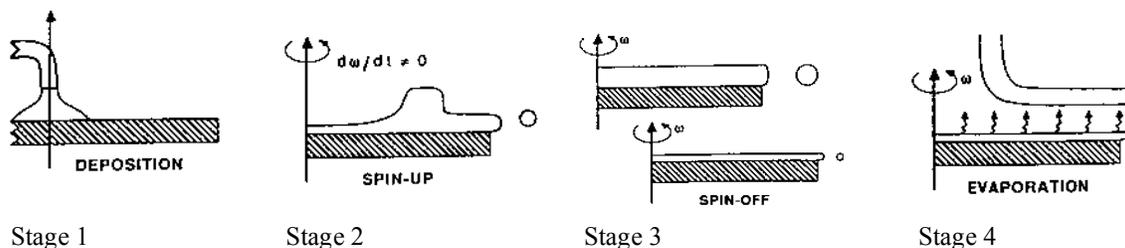


Figure 1. The key stages in spin coating⁴

Spin coating is a process used to distribute material evenly on wafer. However, when the coating is relatively thin and high-aspect features, such as contact holes, are patterned in different pitches, the thickness bias between isolated and dense areas still poses a serious problem. Two major things happen during the high-speed spin: 1) material moves across the wafer, and 2) the material phase changes from a thin liquid to a viscous flow material and then to a solid because the solvent evaporate. To study this process theoretically, two extreme conditions are discussed: pure solid and pure liquid.

The assumption of pure solid is the distribution of the material in spin coating is uniform across the wafer, in other words, dense and isolated areas are covered with the same amount of the material. However, the dense area needs more material to fill the spaces in the vias, and, as the result, less material is left to form a top layer above the vias. Because the isolated area contains fewer vias, more material remains on top to form a thicker layer. Figure 2 shows the via structure and relative coating thickness under the pure solid assumption.

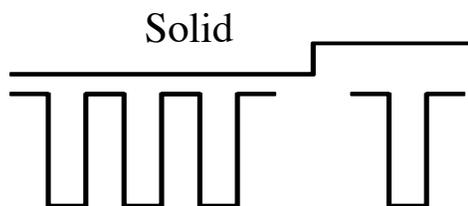


Figure 2. The via and coating structure on isolated and dense areas, assuming the material is pure solid.

In this condition, the bias comes from the via volume difference between isolated and dense areas, which can be written as

$$Bias_{solid} = \frac{\Delta V_{vias}}{S} \quad (1)$$

where ΔV_{vias} is the via volume difference between the dense area and the isolated area, S is the area of the coated region.

In the pure liquid assumption, the material flows very well and the surface will be leveled during spin coating. Figure 3 shows the via and coating structure for this condition.

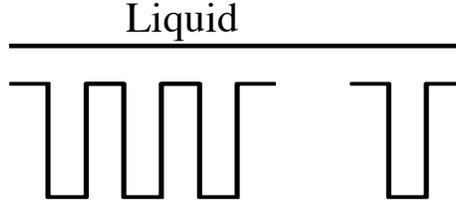


Figure 3. The via and coating structure on isolated and dense areas, assuming the material is pure liquid.

While no bias occurs when the material is spreading over the wafer surface, as Figure 3 shows, the bias will be formed as solvent evaporates from the coating. The dense area contains more solution, and therefore experiences the evaporation of a greater volume of solvent than isolated area does. Thus, the thickness reduction at dense area is more than it at isolated area. This bias can be written as a function of the solid concentration, C_s .

$$Bias_{liquid} = \frac{\Delta V_{vias}(1 - C_s)}{S} \quad (2)$$

A real material is neither pure solid nor pure liquid. Instead, the material is one that undergoes the change from liquid to solid with the evaporation of the solvent throughout entire spin-coating process. The best model should take into the consideration of bias caused by both via volume difference and solvent evaporation. To simplify the calculation, we introduce a parameter a , which is defined as the percentage of liquid-like. Therefore, $1-a$ is the percentage of solid-like. Combining the parts having the two properties in one equation, we have

$$\begin{aligned} Bias &= (1 - a) \frac{\Delta V_{vias}}{S} + a \frac{\Delta V_{vias}(1 - C_s)}{S} \\ &= \frac{\Delta V_{vias}}{S} (1 - aC_s) \end{aligned} \quad (3)$$

From equation 3, we can see a needs to be large, and C_s needs to be large also in order to achieve a small bias. This relationship means the material is more liquid-like but contains less solvent. A solvent with high boiling point evaporates slowly, which keeps the material in the liquid phase longer, but more solvent will remain in the film when solvent evaporation dominates the coating thinning behavior. A solvent with low boiling point evaporates more quickly, which produces a drier film, but the material stays in the liquid-phase for less time and therefore stops moving quickly. The ideal material for planarizing a surface would remain in the liquid phase during the spin-coating process and experience no shrinkage due to solvent evaporation or other reactions. Good candidates are low viscous monomers or small molecules materials that can be coated without solvent. However, these kinds of materials always pose problems related to coating quality, thickness control, and wafer handling.

2.2 Bake

Most BARCs and gap-fill materials are thermosetting polymer systems. During high temperature bake, two events occur simultaneously. One is polymer thermal reflow, and the other is the crosslinking reaction. Polymers used in thin

film coatings usually have T_g between 20°C and 150°C. When the film curing temperature is above polymer's T_g , the polymer becomes viscous and is able to reflow. This thermal reflow smoothes the surface and reduces the bias formed during spin coating. At the same time, crosslinking takes place that stops the movement of the polymer. We will now consider rheology and chemical reaction kinetics as we discuss polymer thermal reflow and the limitation of flow time due to crosslinking.

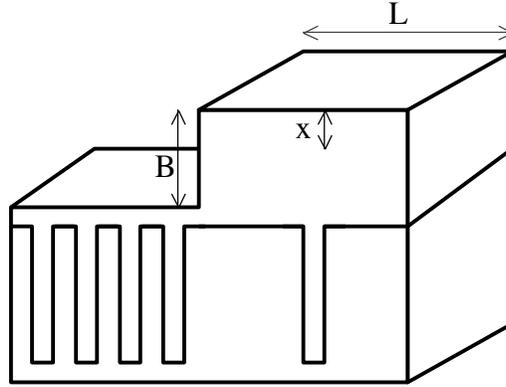


Figure 4. The bias model.

Figure 4 is the scheme of the bias model after spin coating, where L is the length of coating area, B is the initial bias formed from spin coating, and x is the reduction in bias resulting from thermal reflow process at high temperature bake. The general viscosity relation is shear stress over shear rate:

$$\eta = \frac{\alpha}{\dot{\gamma}} \quad (4)$$

Shear stress is the force that causes the movement. In this case, the force is the gravity, that is the material at higher altitude with higher potential will move down. The shear stress is given by

$$\alpha = \frac{F}{S} = \frac{mg}{S} = \frac{(B-x)S\rho g}{S} = (B-x)\rho g \quad (5)$$

where F is the force, S is the area of isolated region, ρ is the material density, and B and x are defined in Figure 4.

Shear rate is strain over time. In this case, shear strain is percent of deformation, which can be expressed as

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{dx}{L} \frac{1}{dt} \quad (6)$$

Upon substituting equations 5 and 6 in equation 4, the viscosity becomes

$$\eta = (B-x)\rho g L \frac{dt}{dx} \quad (7)$$

In equation 7, t is the time that the polymer is able to flow, which is determined by the speed of the chemical reaction corresponding to the formation of an infinite network. We know the reaction rate is the function of the concentration of crosslinking sites, reaction order, and a rate constant derived from the Arrhenius equation.

$$\frac{dC}{dt} = -Ae^{-E/RT} C^n \quad (8)$$

where A is a constant specific to each reaction, E is the reaction activation energy, n is the reaction order, C is the concentration of crosslinking sites. The viscosity can be rewritten as a function of dC and dx with time dt defined by equation 8.

$$\eta = -\frac{(B-x)\rho gL}{AC^n e^{-E/RT}} \frac{dC}{dx} \quad (9)$$

Viscosity and the concentration of crosslinking sites are not constants and are changing with the reaction. The Crosslinking reaction links polymer chains together, which results in an increase in polymer molecular weight and the formation three-dimensional network.⁵ The length of the polymer chain plays a significant role in determining the resistance to flow and affects viscosity η . Because the length of the polymer chain is indicative the molecular weight, the relationship of viscosity and molecular weight is a power function, where the power, m , in the equation 10 is approximately 3.4 – 3.7 for most polymers. The relationship of molecular weight and crosslinking sites is complex, which may be derived from statistical approach.⁵ Here, we use a simple expression with the power m' instead of m .

$$\frac{\eta}{\eta_0} = \left(\frac{M}{M_0}\right)^m = \left(\frac{C_0}{C}\right)^{m'} \quad (10)$$

Also, viscosity is a function of temperature, so, the temperature dependence of η can be expressed in the form⁶

$$\eta_0 = \eta_\infty e^{E_\eta/RT} \quad (11)$$

where η_∞ is a constant, and E_η is the activation energy required to create a space big enough for a molecule to transfer during flow. We can establish the viscosity based on equation 10, 11, and 12

$$\eta = \eta_0 \left(\frac{C_0}{C}\right)^{m'} = \eta_\infty \left(\frac{C_0}{C}\right)^{m'} e^{E_\eta/RT} \quad (12)$$

Equation 9 is derived from rheology, and equation 12 is derived from chemical reaction and temperature dependency. Combining them in one equation, we obtain

$$\eta_\infty \left(\frac{C_0}{C}\right)^{m'} e^{E_\eta/RT} = -\frac{(B-x)\rho gL}{AC^n e^{-E/RT}} \frac{dC}{dx} \quad (13)$$

If $B-x \neq 0$, the term can be moved to one side of the equation with dx , and the terms related to the concentration of crosslinking sites C can be moved to the other side of the equation.

$$\frac{1}{(B-x)} dx = -\frac{\rho gL C^{m'}}{\eta_\infty C_0^{m'} e^{E_\eta/RT}} \frac{1}{AC^n e^{-E/RT}} dC \quad (14)$$

To get the expression of the bias $B-x$, we need to integrate both sides of equation 15 from initial condition to the end condition. At the beginning of bake, the distance the material moves is 0 and the initial concentration of crosslinking sites is C_0 . At the end of the process, the material moves to X position and the polymer is in a gelation state. Using a statistical approach, the gel point can be derived by calculating when the average molecular weight approaches an infinite size. Assuming the critical extent of the reaction at gel point is P_c , the concentration of crosslinking sites at that time should be $C_0(1-P_c)$.⁵ To simplify the calculation, we consider P_c equates to 1.

$$\int_0^x \frac{1}{(B-x)} dx = \int_{C_0}^0 -\frac{\rho gL C^{m'}}{\eta_\infty C_0^{m'} e^{E_\eta/RT}} \frac{1}{AC^n e^{-E/RT}} dC \quad (15)$$

$$[-\ln(B - X)]_0^X = \left[-\frac{\rho g L C_0^{1-n+m'}}{A \eta_\infty C_0^{m'} (1-n+m')} e^{\frac{(E-E_\eta)}{RT}} \right]_{C_0}^0$$

$$bias = B - X$$

$$bias = B \exp\left(\frac{-\rho g L C_0^{1-n}}{A \eta_\infty (1-n+m')} e^{\frac{(E-E_\eta)}{RT}}\right) \quad (16)$$

This equation contains parameters related to polymer rheology and chemical reaction, and is full of information about what properties a material should have in order to achieve a low bias. Table 1 shows the definition of all parameters in equation 16 and their design values.

Table 1. Definition of the parameters in equation 16 and their design values for achieving low bias

Field	Parameter	Definition	Design
Spin coating	B	Bias formed by spin coating	Low
Chemical reaction	E	Activation energy of reaction	High
	A	Reaction constant	Low
	n	Reaction order	-
	C ₀	Concentration of crosslinking site	-
		If n>1	Low
	If n<1	High	
Polymer rheology	E _η	Activation energy of viscosity	Low
	m'	Viscosity change with crosslink	High
	η _∞	Viscosity at infinite	Low
Temperature	T	If E - E _η > 0	Low
		If E - E _η < 0	High

At the first, bias formed in spin coating needs to be low. As discussed in section 2.1, the materials that have a better flow property and less solvent evaporation will produce a smaller bias. However, these two terms usually work against each other because of the physical nature of spin coating. Spin coating condition such as spin speed, acceleration, and air flow may have effects on the initial bias, but the improvement is usually not significant.

The crosslinking reaction must be slow and the activation energy must be high. For most reactions, reaction order n is equal to or large than 1, so that the concentration of crosslinking sites needs to be low. In other words, the difficult and slow crosslinking reaction will give the polymer more time to flow. Also, if a material has a high gelation point (high P_c), such as low molecular weight polymer, it helps the material stay flowing longer time. Low polymer melting viscosity is important for thermal flow. Hence, low T_g polymers are the better candidates for planarizing. Temperature could vary directions depending on whether $E - E_\eta$ is positive or negative. We will discuss temperature effects in detail in the next section.

3. EXPERIMENTS

Two planarizing BARCs, ARC81 and DUV52, have been chosen for the temperature dependency study because the polymer platforms of these two products are very different. Samples were spin coated onto the wafers at 1500 rpm for 60 seconds and then baked at different temperatures. The samples' solid concentration had been adjusted to keep all coating thicknesses nearly equal. The substrate used in the study is a SiO₂ wafer with contact holes patterned by IMEC. The vias were 1μm deep, 0.22μm wide, and the pitches ranged from 1:1 line/space dense to isolated vias.

Table 2. Iso/dense bias of ARC81 and DUV52 at different bake temperatures.

Bake temperature (°C)	Iso/dense Bias (nm)	
	ARC81	DUV52
225	-	245
205	274	246
175	263	256
150	242	274
135	248	331

From the iso/dense bias data of two samples listed in Table 2, we see two different trends related to temperature. The bias of ARC81 decreases with a decrease in temperature, while the bias of DUV52 increases with a decrease in temperature. As equation 16 describes, ARC81 is the type of material having $E - E\eta < 0$, and DUV52 is type of material having $E - E\eta > 0$. To prove this concept, we set up a series of experiments to determine activation energies E and $E\eta$.

Viscosity activation energy can be easily determined by equation 12. Figure 5 shows the curves representing the viscosity of the polymers versus temperature, as measured on an AR2000 Rheometer (TA Instruments). Their fitted trend lines show $E\eta$ of DUV52 polymer is 10 times larger than $E\eta$ of ARC81 polymer. Increasing the temperature did not change the viscosity of ARC81 polymer much, but it brought down the viscosity of DUV52 polymer a lot.

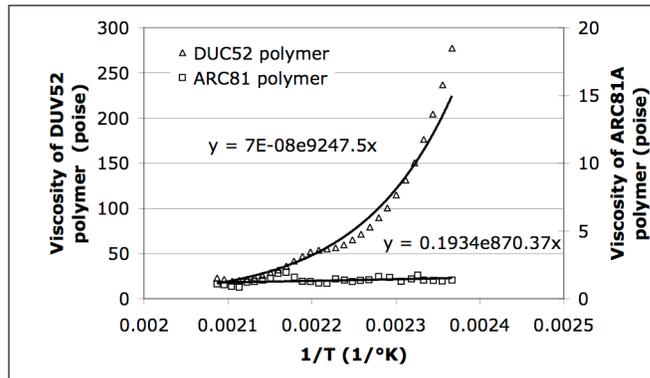


Figure 5. The polymer viscosity changes in the temperature range of 150°C to 208°C.

Measuring the activation energy of the reaction is difficult because the crosslinking reaction happens too fast. Figure 6 is another set of Rheometry data resulting from tests conducted using the condition of 10°C/min temperature ramp.

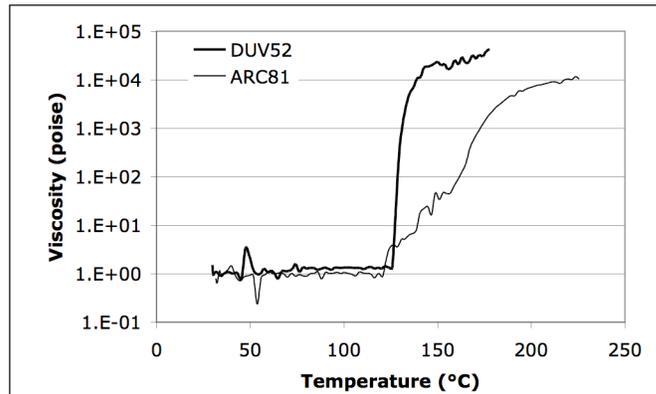


Figure 6. The viscosity of the full formulation changed sharply due to the crosslinking reaction.

In Figure 6, two samples show sharp transition on viscosity curves when crosslinking reactions take place. The reaction of DUV52 started at 126°C and finished within 2 minutes across 20°C. ARC81 starts to react at the same temperature, but the viscosity increased slowly and turned flat at about 200°C. In bake temperature range of 150°C to 225°C, increasing temperature did very little to the DUV52 reaction, but it accelerated the ARC81 reaction.

4. CONCLUSION

Spin coating is the application method that distributes material on the wafer evenly, but iso/dense bias still exists in dual damascene applications due to the via volume differences and solvent evaporation. Two ideal conditions have been modeled mathematically. We can conclude that the coating material needs to be more liquid-like but contain less solvent, which is difficult to achieve in the real world. High temperature baking gives the polymer a chance to reflow and thus smooth the surface. We calculated how far the material is able to reflow before it forms an infinite network. The result gave us an indication of how a polymer's Rheology properties and chemical reaction affect the bias reduction during high temperature baking. DUV52 and ARC81 are good examples for showing how temperature could affect the bias in different ways depending on the activation energy of chemical reaction E and viscosity $E\eta$.

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