# Development of novel UV cross-linkable materials for enhancing planarity in via applications via the correlation of simulated and experimental analyses

Satoshi Takei<sup>1\*</sup>, Michael W. Lin<sup>2</sup>, Sangwoong Yoon<sup>1</sup>, Tomoya Ohashi<sup>1</sup>, Yasuyuki Nakajima<sup>1</sup>, C. Grant Willson<sup>2</sup>

<sup>1</sup>Nissan Chemical Industries, Ltd, Toyama Japan <sup>2</sup>The University of Texas, Austin, Texas USA

### ABSTRACT

The use of conventional thermally cross-linked materials in advanced lithography and nano-imprinting techniques, such as negative photo resist, anti reflective coatings and planarizing layers, does not guarantee that a high degree of planarization will be obtained. Additionally, iso-dense thickness biases can create problems by narrowing process latitudes.

This presentation focuses on the correlation between simulated and experimental analyses and how planarization is affected. The factors we have identified that influence a material's planarizing capability are; coating spin speed, spin time and the relationship between the solvent concentration of the material and it's via filling properties. Through optimization of these factors, an appreciable reduction in via topography was achieved. Based on our results, novel, UV cross-linkable materials have been developed and optimized for improving planarity in via applications.

Keywords: UV cross-linkable materials, coater, planarization, lithography, imprint

## **1. INTRODUCTION**

The degree of the integration in the semiconductor device has been increasing, which requires the development of new techniques not only in the light source and materials in the lithography but also in the conduction materials used for the connection of layers prepared by the above iterative processing, interlayer dielectric films as insulator, and so on. In addition, these new techniques should be less expensive in the actual application.

Moreover, several problems that could be ignored before are pronounced with the down-sizing of the device. For example, the simulation of planarization for lithography processes was not well understood, and then the methods for designing materials and developing suitable coating processes for planarization were very "misty. In special, the production of the bumpy surface is an important technique in the semiconductor manufacturing process<sup>1</sup>. To attain this, gap fill material is placed between the resist and the substrate<sup>2-3</sup>. The gap fill materials should realize; (a) excellent planarization on the substrate surface having irregularities such as via and step for patterning and etching as shown in Fig. 1, (b) void free filling in the via for substrate etching, and should have (c) matched etch rate to SiO<sub>2</sub> based interlayer dielectric films for substrate etching.



Fig. 1. Comparison of conformal and planar coating on the substrate surface having irregularities.

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In addition to above conditions, gap fill material under resist should be cross-linked after it is pasted on the Si surface to avoid the inter-mixing with the resist materials. And, the materials are required to be kept with low metal concentration in solution (less than ppb level) and low nano-level defect number for substrate etching.

The purpose of this study is to develop the new UV cross-linkable materials and coating methods for enhancing planarity in via applications in advanced lithography and nano-imprinting processes. We reported the correlation between simulated and experimental analysis using UV cross-linkable gap fill materials, and the films performance.

### **2. EXPERIMENTAL**

In the correlation between simulation and experimental analysis, UV cross-linkable gap fill material UVM60 consisted of liquid materials with different molecular weight and photo acid generator were developed, as shown in Fig. 1. UVM60 had no solvents to ignore the evaporation in spin coating process (UVM60 density; 0.9 g/ml, viscosity 34 cP, surface tension; 36.5 dyne/cm, film shrinkage; 6.3 %).



Fig. 2. Liquid raw materials with two different molecular weights in UVM60.

And, in the evaluation to obtain the controlled thickness and the uniformity on 300 mm wafer, UV cross-linkable gap fill material with solvents such as propylene glycol monomethyl ether (boiling point: 121 °C), and propylene glycol monoethyl acetate (boiling point: 146 °C), photo acid generator with a molecular weight range of 900-1100 and a melting point of 130 °C, and additives for sublimation, optical properties and resist poisoning reduction was developed and named UVM60S.

The UV cross-linkable process, ultra violet exposure treatment tool, and step pattern wafers are shown in Fig.3. The spin-coat condition was 1000-5000 rpm for 20-30 s, and then the materials were irradiated by expose wavelength of 200-400 nm with 10-100 mJ/cm2 and 23 °C under air gas conditions. After UV irradiation, the wafers were baked on a hot plate with 100 °C for 60 s. The spin coating conditions in the correlation between simulation and experimental analysis were shown in Table 1.



Fig. 3. Spin-coating process((a): UV cross-linkable process, (b): step pattern wafers).

Table 1. Spin coating conditions in the correlation between simulation and experimental analysis.

<u>No.</u>	Speed (rpm)	Thickness (µm)	Width (µm)
Run-A1	<u>2000</u>	2	250, 100, 50
Run-A2	<u>3000</u>	2	250, 100, 50
Run-A3	<u>4000</u>	2	250, 100, 50
Run-A4	<u>5000</u>	2	250, 100, 50
Run-B1	2000	<u>5</u>	250, 100, 50
Run-B2	2000	<u>4</u>	250, 100, 50
Run-B3	2000	<u>3</u>	250, 100, 50
Run-B4	2000	1	250, 100, 50

In simulation setup, the thickness bias was calculated using to equation (1) and  $(2)^{1,4-6}$ .

Thickness bias 
$$\propto \Omega^2$$
 (1)  

$$\Omega^2 = \frac{\rho \omega^2 w^3 r_o}{\gamma h_o} \quad (2)$$

 $\Omega^2$  is a ratio between centrifugal and capillary forces. Decreasing  $\Omega^2$  increases the film planarity, therefore, it should theoretically decrease the iso-dense bias ( $\rho$ ; density,  $\gamma$ ; surface tension,  $\omega$ ; spin speed, W; feature width, ho; film thickness,  $r_o$ ; radial position of feature).

# 3. RESULTS AND DISCUSSION

3.1. Correlation between simulation and experimental analysis in UVM60

Figure 4 shows (a) the dependences of spin speed and (b) film thickness on the thickness bias. And, the dependences of  $\Omega^2$  on the thickness bias over isolated trench and line were calculated as shown in Fig. 5.



Fig. 4. Dependences of (a) spin speed and (b) film thickness on the thickness bias over isolated trench and line.



Fig. 5. Dependences of  $\Omega^2$  on the thickness bias over isolated (a) trench and (b) line.

Thickness bias increased as spin speed increased because  $\omega$  increased. On the other hand, the thickness bias decreased as film thickness increased because  $h_0$  decreased. These experimental results seemed to be matching-up the trends by the simulation. It was considered that UVM60 behaves like a newtonian nonvolatile fluid for a range of spin speeds and thicknesses.

### 3.2 Planarization in UVM60S

The performances of planarization in UV cross-linkable gap fill material UVM60S and thermal cross-linkable gap fill material are shown in Fig. 6. It was obtained that the thickness bias of blanket-200 nm dense in UVM60S had only 12 nm (= 420 - 408 nm) and the thickness bias of blanket-900 nm dense had 60 nm (= 420 - 360 nm) in 420 nm blanket field thickness. The planarization of the film obtained from UVM60S was very high as compared with that of the film obtained from thermal cross-linkable gap fill material as the reference.



Fig. 6. Comparison of planarization in (a) UVM60S and (b) thermal cross-linkable gap fill material.

These results indicate that the compositions such as base-resin for forming UVM60S with liquid phase as main composition at room temperature were smoothly poured into a plurality of holes also in the dense portion in which the number of holes per unit area on the via substrate (the hole density) is larger than that of the blanket field. This has led to a small difference between the film thickness of the blanket field and that of the dense portion and to a large planarizing factor by using novel approach of UV cross- linkable process.

It was considered that excellent planar property in UVM60S can do the integration test without etching back process after coating on via pattern for dual damascene process. In addition, 2nd coating BARC and gap fill material in double patterning process, and the new application to need planarization can be expected to evaluate the film properties as sacrificial and the permanent materials.

## **4. CONCLUSION**

This study focused on the correlation between simulation and experimental analysis using UV cross-linkable gap fill materials for planarization in advanced lithography and nano-imprinting techniques. In the characterization of UV cross-linkable gap fill materials, two key factors were identified. The factors were the specific dependence of planarization on the spin-speed and film thickness. By optimizing these factors, an appreciable reduction in via topography was realized. A novel gap fill material UVM60S has been optimized and developed for excellent planarization properties. In this study, the planarization of UVM60S was shown to be better performance than that of thermal cross-linkable gap fill material.

#### REFERENCES

- [1] M. W. Lin, B. Chao, J. Hao, K. Osberg, P. S. Ho, and C. G. Willson, Journal of Micro/Nanolithography, MEMS, and MOEMS 7(1) (2008).
- [2] S. Takei, Y. Sakaida, T. Shinjo, K.Hashimoto and Y.Nakajima, Proc. SPIE 6923, 69232P (2008).
- [3] S. Takei, Proc. SPIE 6519, 65192V (2007).
- [4] L. E. Stillwagon, and R. G. Larson, Proc. Electrochemical Society 90-1, 230-8 (1990).
- [5] L. M. Peurrung, and D. B. Graves, Journal of the Electrochemical Society, 138(7), 2115-24 (1991).
- [6] P. Y. Wu, F. C. Chou, and S. C. Gong, Journal of Applied Physics, 86(8), 4657-4659 (1999).
- [7] L. E. Stillwagon, and R. G. Larson, Proc. Electrochemical Society 90-1, 230-8 (1990).
- [8] L. M. Peurrung, and D. B. Graves, Journal of the Electrochemical Society, 138(7), 2115-24 (1991).