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Thin Solid Films 500 (2006) 214 – 218
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Fullerene-incorporation for enhancing the electron beam resist performance for contact hole patterning and filling

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Received 4 May 2005; received in revised form 2 November 2005; accepted 2 November 2005

Abstract

The fullerene molecules such as C60 and C70 were incorporated in the commercial positive electron beam resist to investigate the performances for patterning and filling the contact holes at nanometer scale. The sensitivity, process window and contrast of the modified resist were improved, while the toluene dilution degraded the sensitivity. The electron beam dose affected the designed holes dimension, and the adulterated resist could print sub-50 nm holes pattern. We found the small amount (0.01–0.02% w/v) of fullerene molecules very effectively promoted the etch resistance and selectivity under fluoro-containing gases, and minimized the film stress. The etching resistance for C60 and C70 modification could be improved by 65% and 68%, respectively. Together with the fullerene-incorporated resist and the etching processes, the sub-50 nm contact hole could be achieved. In addition, the gap-filling and step coverage capability of titanium nitride into nanometer contact hole with chemical vapor deposition was better than physical vapor deposition.

Keywords: Fullerene molecule; Electron beam resist; Contact hole patterning; Filling capability

1. Introduction

During the past two decades, there has been an extremely rapid growth in both the technology and the application of microelectronics, to the point that it now pervades virtually all aspects of commercial and military business. The size and performance of microelectronic devices have been improved substantially, especially in the past few years [1,2]. In the updated International Technology Roadmap for Semiconductors [1], the 50 nm contact hole in the resist will be used in year 2011. In general, photoresists are not suitable for patterning the contact holes at nanometer scale, except for strict process control and resolution enhancement techniques, such as phase-shifting mask, optical-proximity correction, and off-axis illumination techniques. The electron beam direct writing (EBDW), in comparison with optical lithography, is a promising means for controlling and patterning small features, down to nanometer scale [3]. This technology has a cost advantage for production volumes below 100 lots in the future [3]. In EBDW, the Gaussian beam has better resolution than shaped beam. But, the shaped beam has an at least 10-fold higher throughput than Gaussian beam due to imposing several pixels per shot [4]. In order to achieve the better resolution and high throughput for shaped beam technology, the utilization of thin resist film is inevitable [5]. However, the application of thin resist film in the shaped electron beam exposure still faces the challenge of poor etching resistance and throughput.

Nano-scale molecules are a possible means to solve the problem of low etching resistance and enhance the lithographic performance for the thin resist film generation. The molecules have the advantages of sub-nanometer size, thermal stability, plasma stability and high electron affinity, and can be incorporated into the resist to alter its performance. Ishhi et al. [6] have used fullerene molecule (i.e., 5 wt.% C60) to modify positive resist, and found the fullerene can enhance the etching resistance while not altering the sensitivity. In addition, they claim that the negative chemically amplified resist incorporated with 3 wt.% C60 exhibits strong environmental stabilization in post-exposure delay. In the latter report [7], they find the resist sensitivity is degraded by the C60 due to the dissolution-

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doi:10.1016/j.tsf.2005.11.040

inhibiting effect. Dentinger and Taylor [8] spike 7.9 wt.% C60 into poly(methylmethacrylate) resist, and the etching resistance is promoted 8% and 26% for CF_4 and Cl_2 plasmas, respectively. However, the use of 3–7.9 wt.% C60 in the resists and the deterioration of resist sensitivity elevate the fabrication cost and restrict the further application of this technology.

In this study, the sensitivity curve of resists after spiking with C60 and C70 molecules is investigated. The film stress, etch resistance and the effect of shaped electron beam dose on the contact hole sizes are carefully studied. In addition, the titanium nitride gap-filling and step coverage on contact holes by 0.02% w/v C70-incorporated resists are also evaluated.

2. Experimental details

The fullerene molecules of C60 and C70 were purchased from Alfa Aesar Company. The toluene solvent was obtained from E. Merck (Darmstadt, Germany). The DSE-1010 positive resist used in this study was obtained from DONGJIN Chemical Co., Ltd. (Korea). There are four types of resist samples in this study, named DSE, DSE+Toluene, DSE+C60, and DSE+C70, respectively. The DSE means the DSE-1010 resist without any modification. The "DSE+Toluene" means the mixture of 50 mL DSE-1010 resist and 50 mL toluene solvent. For the "DSE+C60-0.01%" sample, 0.01 g C60 fullerene is first dissolved in 50 mL toluene, and then mixes with 50 mL DSE-1010 resist. The final concentration of C60 molecule in the resist is 0.01% w/v. In the same manner, the "DSE+C70-0.02%" uses 0.02 g C70 fullerene to prepare the sample.

Electron beam exposure was performed on a Leica Weprint 200 stepper. The electron beam energy was 40 keV, and the beam size was 20 nm. The developer for the electron beam resist was an aqueous 2.38% tetramethylammonium hydroxide (TMAH) solution. A positive-tone electron beam resist was spin-coated on a silicon wafer (150 mm diameter) and baked at 95 °C for 120 s. After exposure and a post-exposure bake (115 °C for 120 s), the wafer was developed using the TMAH solution for 60 s. Again, a hard-bake was applied to the wafer (115 °C for 120 s). Critical dimensions were evaluated using either an in-line scanning electron microscope (SEM, Hitachi S-6280) or a cross-sectional SEM (Hitachi S-4000). The stress of resist film was measured by TENCOR FLX-2320 instrument. In the stress measurement, the curvatures of bare silicon wafers, resist-coated wafers were determined.

Silicon dioxide film was etched using a reactive-ion etcher (RIE, Tokyo Electron Limited, Model TE5000, Japan). There are two steps for silicon dioxide etching. The operating conditions for step 1 are: 0.2 Torr pressure, 0 W RF power, 400 $cm^3\ min^{-1}$ Ar gas, and etching gases of CHF_3 and CF_4 ($CHF_3+CF_4=40\ cm^3\ min^{-1}$). The operating conditions for step 2 are: 0.2 Torr pressure, 500 W RF power, 400 $cm^3\ min^{-1}$ Ar gas, and etching gases of CHF_3 and CF_4 ($CHF_3+CF_4=40\ cm^3\ min^{-1}$).

The thermal oxide was grown under dry O_2 at 900 °C in quartz reactor to a thickness of 100 nm. After coating the fullerene-incorporated resist onto the thermal oxide and resist patterning, the plasma process of mixing CHF_3 and CF_4 gases was used to etch the underlying silicon dioxide layer. Then, the contact holes defined by 0.02% w/v C70-incorporated resist were deposited with the titanium nitride (TiN) plug by physical vapor deposition (PVD) and chemical vapor deposition (CVD). The TiN PVD sputter system (ULVAC SBH-3308 RDE system) was used to deposit 200-nm TiN film, and argon and nitrogen were used as process gases. For the film deposition by CVD method, the tool from Materials Research Corporation (MRC) was used to deposit TiN film by gas mixture of $TiCl_4$ and NH_3 at 630 °C. The chemical reaction is as follows: $6TiCl_4+8NH_3 \rightarrow 6TiN+24HCl+N_2$.

3. Results and discussion

3.1. Enhancement of lithographic performance

In the electron beam writing technology, positive-tone resist is usually used to fabricate the contact hole [3]. In this study, the commercial DSE-1010 electron beam resist is a positive type, and the fullerene molecules such as C60 and C70 are incorporated into the commercial resist. Fig. 1 depicts the resist sensitivity curve. The irradiation dose (D_i) for the "DSE" resist that the acid generator and functional group in the polymer begins reaction is 2.3 $\mu C/cm^2$, while the dose (D_c) that the polymer film can fully dissolve is 3.4 $\mu C/cm^2$. As to the "DSE+Toluene" sample, both D_i and D_c are increased. This observation is attributed to the dilution of acid generator by toluene solvent, and therefore, reduces the sensitivity. Interestingly, the sensitivity for 0.01% w/v "DSE+C60" or "DSE+C70" sample is significantly enhanced after spiking the fullerene molecules. Both D_i and D_c are decreased to 1.4 $\mu C/cm^2$ and 2.2 $\mu C/cm^2$, respectively. This finding suggests that the incorporation of fullerene molecules into resist can effectively enhance the process throughput.

What happens to the decrease of addressing dose for the resist after spiking with fullerene molecules? In the resist, the electron beam activates the bond of acid generator to produce acid, and the acid induces the functional group reaction of the polymer. The irradiated electron beam easily penetrates

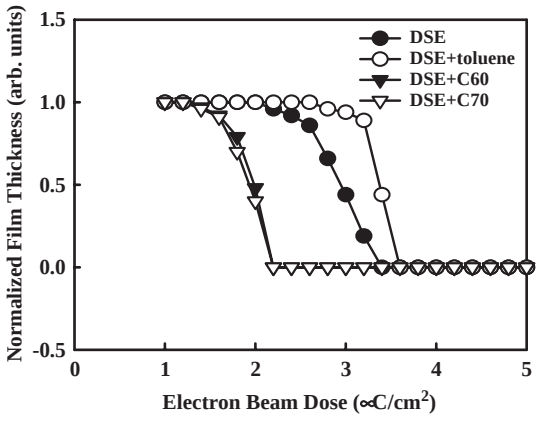

Fig. 1. The effect of the electron beam dose on the normalized resist film thickness.

through the void region embedded in the resist film, and degrades the throughput. We infer that the fullerene molecules with sub-nanometer sizes (0.7–0.8 nm) are embedded into the void of resist sample (in Fig. 2). The C60 or C70 fullerene embedded in the void region has a higher electron affinity ~2.6 eV, and therefore, facilitate the bond activation for the acid generator. As we know that the electron accelerating voltage can influence the sensitivity, the higher accelerating voltage can improve the resist resolution but deteriorate the resist sensitivity [4]. However, the incorporation of fullerene molecules can shorten the resist exposure time.

Fig. 3a indicates that the hole dimension is significantly influenced with the exposure dose, while the fullerene-incorporated resists in Fig. 3b and c are not. The resist without embedded fullerene molecules cannot resolve 60 nm contact hole. The electron beam doses at 7 μC/cm^2 and 8.5 μC/cm^2 can resolve 50 nm contact hole for the resist with 0.01% C60 and C70 modification, respectively. We define the dose range for the "nominal hole ± 10% x (nominal hole)" as the process window. The fullerene-incorporated resists have wider dose windows (i.e. 8–9.5 μC/cm^2 for 0.01% C60, and 9.5–11.5 μC/cm^2 for 0.01% C70) for 60 nm contact hole formation than unadulterated resist. These phenomena are all attributed to the high electron affinity of fullerene molecules.

The C70 fullerene molecule is chosen for further studies due to its better process window. The SEM images for the resist with 0.01% w/v fullerene modification are illustrated in Fig. 4. The fabrication yield of 60 nm nominal hole in Fig. 4a is not satisfactory due to the lack of electron affinity fullerene. Fig. 4b demonstrates that the resist with C70 fullerene molecules can resolve 53 nm hole. The stresses for various fullerene-incorporated films from three replicates are shown in Fig. 5. The resist film without spiking fullerene has large compressive stress (~1.52 GN/m^2). The stress for "DSE+Toluene" sample also has larger value of 1.1 GN/m^2. However, the spiking of fullerene molecules such as C60 or C70 can effectively minimize the stress to less than 0.1 GN/m^2, and is beneficial to the surface flatness in multilayered wafer exposure. The reason also attributes to the fullerene embedded into the void of the electron beam resist.

3.2. Enhancement of etching performance

The reactive-ion etcher is used to evaluate the etching resistance for the fullerene-incorporated resist on a silicon dioxide layer. The feeding gas is a mixture of Ar, CHF_3, and CF_4. Although it is not illustrated here, the etching rates of these resists and the oxide film both decrease upon increasing the CHF_3 content. This observation explains the role CHF_3 in the plasma. The species generated from CHF_3 in the plasma are H^+ and CF_3^-, and the CF_3^- species can quench the activity of CF_3^+ in the plasma. Hence, the etching rate decreases. Fig. 6 depicts the etching selectivity for these resists. The selectivity is defined as the etch rate of silicon dioxide film to the resist film. The selectivity gradually increases upon increasing the relative CHF_3 content. In addition, the increase of amount of fullerene molecules can also enhance the selectivity over that of the unadulterated resist. This observation supports the assump-

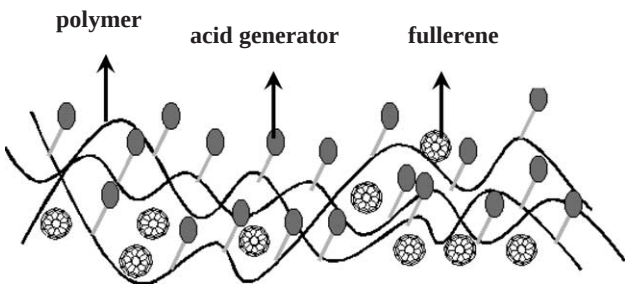

Fig. 2. The model for incorporation of fullerene molecules in the void of resist polymer.

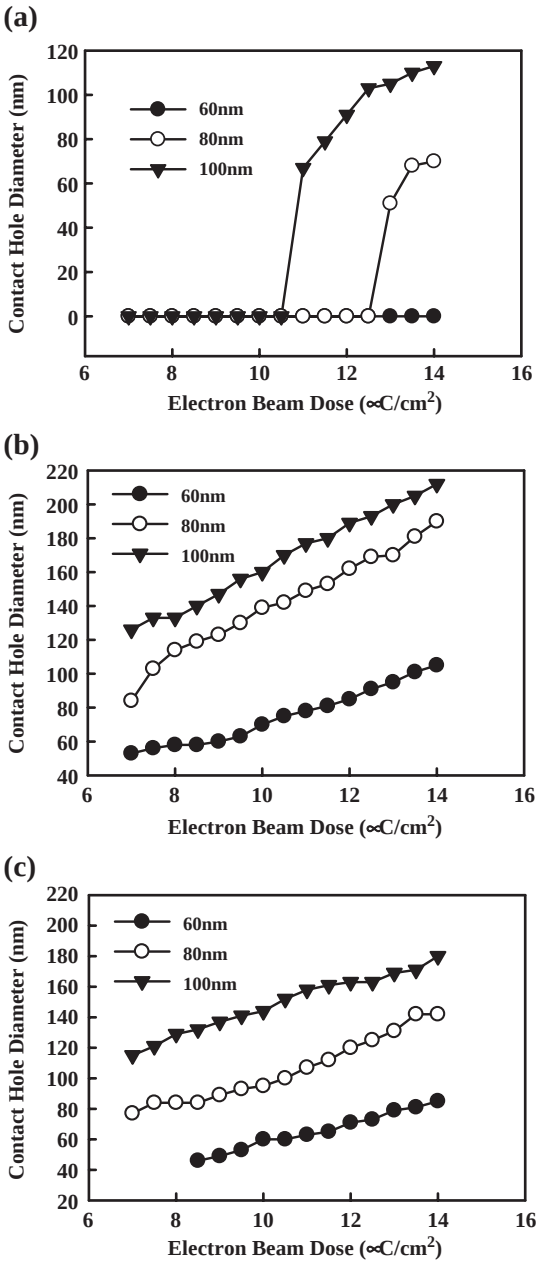

Fig. 3. The effect of electron beam dose on the final hole dimension for target hole dimensions of 60, 80, and 100 nm: (a) DSE resist, (b) DSE resist with 0.01% w/v C60, and (c) DSE resist with 0.01% w/v C70.

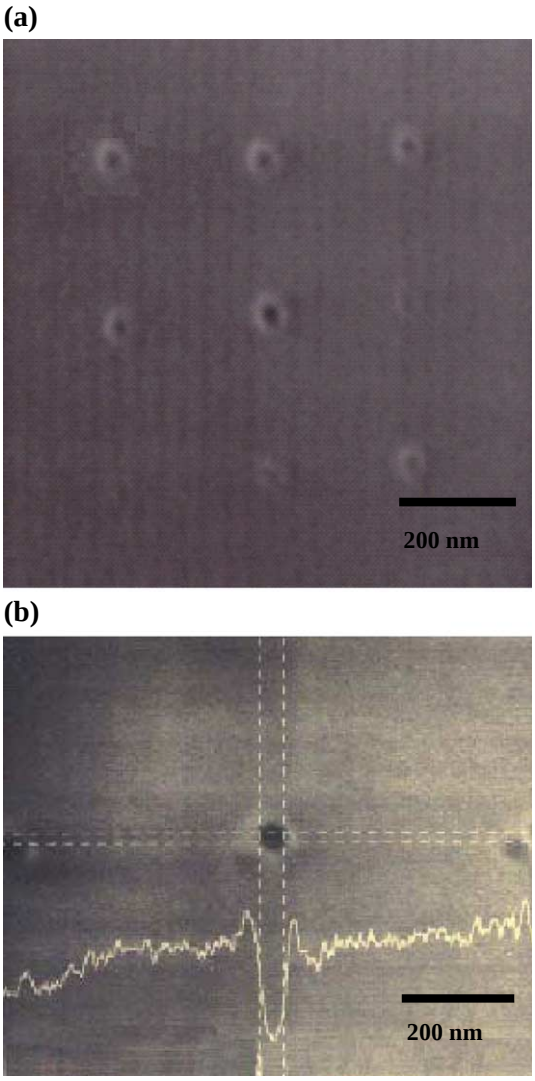

Fig. 4. Top view SEM images of 60 nm nominal hole (a) without and (b) with C70 fullerene in the electron beam resist.

tion that the fullerene molecules can effectively fill the free volume of the resist film. The fullerene molecules consolidate the film, and therefore, the resist film is more resistance to the etching gases. We also find that the incorporation of C70 has better etch resistance than C60. This finding is attributed to the higher molecular weight of C70. It should be noted that the amount of fullerene spiking is only 0.01–0.02%, which is much lower than literature [6–8] report (i.e. 3–50%).

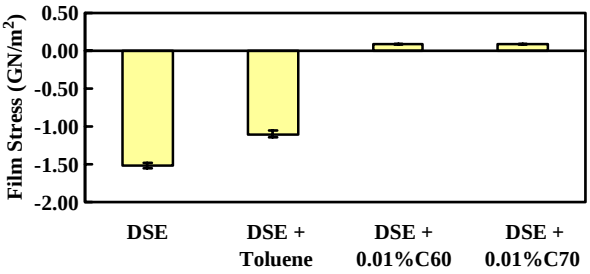

Fig. 5. The stress of resist film ($n=3$) on the silicon wafer.

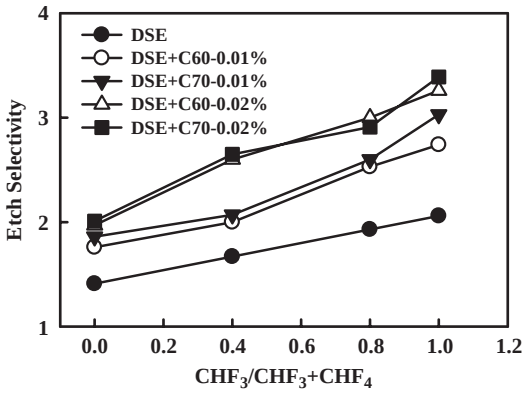

Fig. 6. Etching selectivity of resist with respect to silicon dioxide.

3.3. Application of fullerene-incorporated resists for patterning and filling the contact hole

Fig. 7a depicts that the 56 nm contact hole in the silicon dioxide film can be fabricated by 0.02% w/v C70 fullerene modification. The cross-section SEM in Fig. 7b suggests that the surface diameter of the hole is wider than the bottom

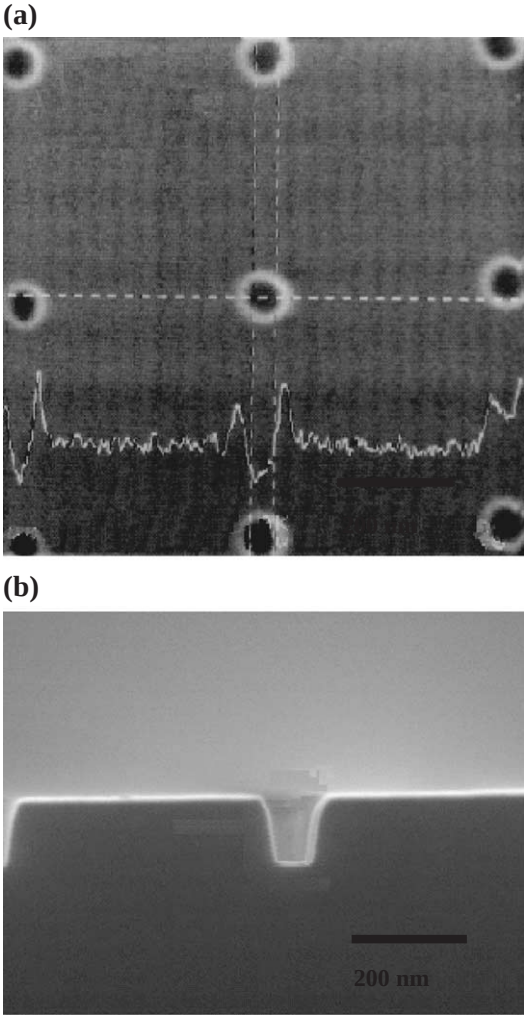

Fig. 7. Top view and cross-section SEM images of a 56 nm contact hole in SiO_2 layer.

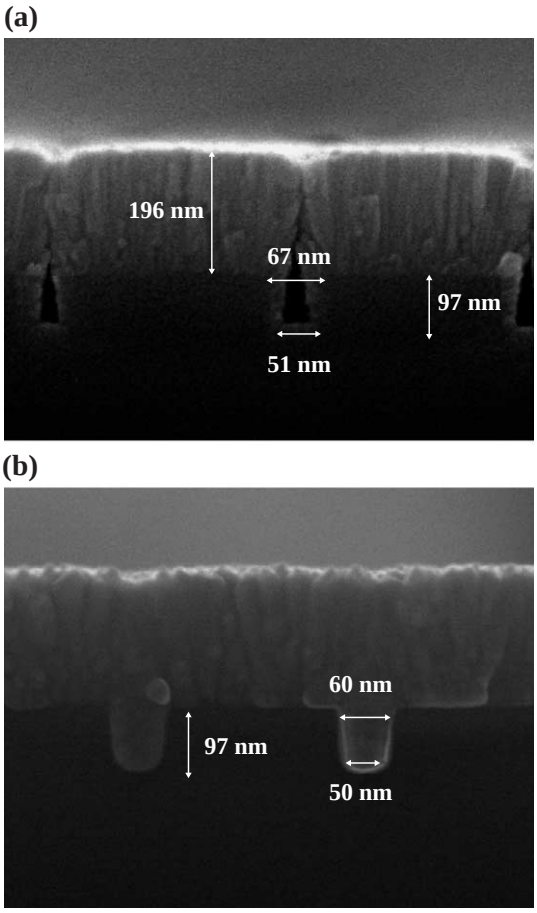

Fig. 8. Cross-section SEM images of ~50-nm contact hole with 200-nm TiN film deposited by (a) PVD and (b) CVD.

diameter of the hole due to reactive-ion plasma etching. The average aspect ratio for the contact hole is ~2. In order to evaluate the hole filling process of TiN plug, the PVD and CVD methods are chosen in this study. The reactive sputtering is used to deposit 200-nm TiN film onto the silicon dioxide pattern. The PVD method uses argon and nitrogen as process gases, and titanium as the target. In plasma, parts of both gases are ionized, and some nitrogen molecules dissociate, which generates chemically reactive free nitrogen radicals. Titanium atoms sputtered off from the target surface by argon ions react with nitrogen when they pass through the argon–nitrogen plasma, and titanium nitride is formed and deposited on the wafer surface. Even some titanium atoms can pass through the plasma and deposit on the wafer surface. They react with nitrogen radicals and form titanium nitride there. Nitrogen radicals can also react with titanium target and form a titanium nitride layer on the target surface. Argon ions sputter the TiN molecules off the target surface and deposit them on the wafer surface. Fig. 8a clearly illustrates that the hole cannot fill with the TiN. The sidewall in the hole is partially covered with TiN, and the surface diameter of hole is thinner than the bottom diameter of hole. The gap-filling and step coverage of the contact hole are not satisfactory by PVD method.

The metal CVD is widely used to deposit metal in IC processing. CVD metal films have proven to be a very good step coverage and to have a gap-filling capability and can fill tiny contact holes to make the connections between metal layers. CVD metal thin films normally have poorer quality and higher resistivity than those of PVD metal thin films. Therefore, they are mainly used for plug and local interconnection and not applied for the global interconnection. Fig. 8b depicts that the nanometer contact hole can be effectively filled by CVD TiN processes without any void problem. These observations from Fig. 8 suggest that CVD method can apply to fill the ~50 nm contact hole.

4. Conclusions

We have established a nanometer fabrication technique that incorporates the small amount of fullerene molecules in the resist for preparing sub-50 nm holes by electron beam lithography. The significant improvement of throughput, resolution, process window, film stress and etch selectivity is attributed to the fullerene's sub-nanometer size, thermal stability, plasma stability and high electron affinity. Together with the above nanofabrication technique, the contact hole at nanometer scale is successfully filled with the CVD TiN. The proposed method can be applied to fabricate the nano-plugs in the future.

Acknowledgment

This work was supported by the NSC-funded national nano-project (NSC 94-2120-M-009-017). The electron beam exposure and measurements were carried out using the facilities located in the National Nano Device Laboratories and National Chiao Tung University.

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