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The novel pattern method of low-*k* hybrid-organic-siloxane-polymer film using X-ray exposure

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Abstract

An organic low dielectric constant (low-*k*) material, hybrid-organic-siloxane-polymer (HOSP), is integrated into multilevel interconnection using X-ray exposure technology. In conventional IC integration processes, photoresist (PR) stripping with O_2 plasma and wet chemical stripper is an inevitable step. However, dielectric degradation often occurs when low-*k* dielectrics undergo the PR stripping process. This limits the application of incorporating low-*k* material into semiconductor fabrication. In order to overcome the integration issue, a novel pattern method, X-ray direct patterning is proposed. In this technology, the dielectric regions illuminated by X-ray will be cross-linked, forming the desired patterns. At the same time, the regions without X-ray illumination are dissolvable in a solvent of HOSP film. Direct-patterning processes have several advantages: (1) they do not need PR to define patterns; thereby the damage from PR stripping can be eliminated, (2) the complex etching on low-*k* dielectrics can be eliminated, (3) the process steps are simplified. In this work, we will investigate the dielectric properties of HOSP film with X-ray curing for the first time. Additionally, a scanning electron microscope image of circle pattern was made to verify the process practicability.

Keywords: Hybrid-organic-siloxane-polymer; Low-*k*; X-Ray; Direct patterning

1. Introduction

As integrated circuit dimensions continue to shrink into ultra large integrated circuit regimes, the interconnect RC delay becomes a serious problem [1]. In order to reduce the RC delay of IC, there is a trend towards using low dielectric constant (low-*k*) materials and copper wiring to replace the traditional SiO_2 and Al in interconnect technology. Among the candidates for low-*k* materials [2–4], spin-on-glass materials have been widely used as interlayer dielectrics in multilevel interconnections because they are easily applied and have relatively low process costs. One of the most promising low-*k* materials is hybrid-organic-siloxane-polymer (HOSP) a hydrophobic dielectric with reasonable mechanical hardness and exceptional thermal and dimensional stability (in excess of 400 °C) [5–7]. In order to integrate copper and low-*k* materials into multilevel interconnects. The damascene process is presently the only option. However, the etching issues and photoresist (PR) stripping are critical during the damascene process (as shown in Fig. 1). The etching process governs the pattern transfer and becomes more difficult as the pattern becomes much smaller. Also, the PR stripping process will damage the low-*k* dielectrics with O_2-based plasma gases [8–10].

The direct patterning with X-ray illumination on low-*k* will solve the above problems and it will be a useful tool in advanced ICs. The advantage of direct patterning is that it can effectively avoid some issues encountered during Cu damascene process. The X-ray lithography process flow is shown in Fig. 2. Using direct patterning technology, the parts of film exposed to X-rays will be cured. The other parts are dissolved in the same solvent used for preparing HOSP film.

In this work, we will discuss the material and the electrical dielectric properties of X-ray exposed HOSP,

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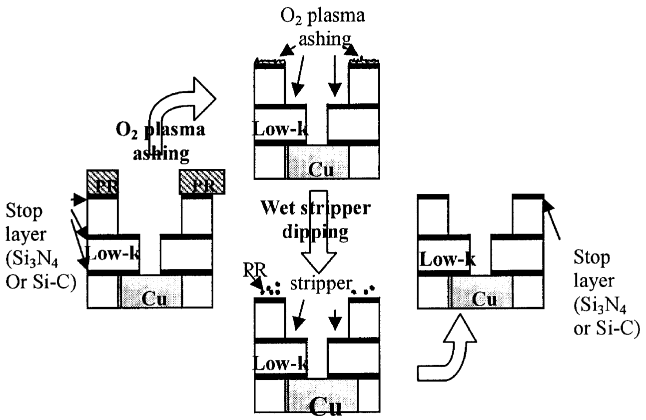

Fig. 1. PR stripping process during manufacturing of damascene process.

and compare them with conventional thermal curing processes. In addition, pattern images will be observed to examine the practicability of using X-ray direct patterning.

2. Experimental

The substrates used in this study were 100 mm p-type (11–25 Ω cm) single crystal silicon wafers with a (1 0 0) orientation. Before film deposition, they were boiled in $H_2SO_4+H_2O_2$ at 120 °C for 20 min to remove particles on surface. These wafers were coated with a low-*k* HOSP solution using two coating stages. In the first stage, spin speed was set 500 rpm and the spinning time was 5 s, and next stage will be rotated at 2500 rpm for 20 s on a model 100 cb spin coater. As-spun wafer was followed by baking on a hot-plate at 150, 200 and 350 °C for 1 min, respectively. It followed that the resultant wafers (as-baked wafers) were transferred to an X-ray exposure system, which is built up at Synchrotron Radiation Research Center (SRRC) in Hsin-Chu, Taiwan, proceeding a curing process. The doses of X-ray illumination were chosen with 10, 20, 30, 40, 50 and 65 W cm^{-2}. Furthermore, a furnace annealing process (at 400 °C, 1 h) was performed on the X-ray exposed wafers to enhance HOSP dielectric properties. On the other hand, in order to investigate the effect of PR stripping during conventional manufacturing process, some of as-baked wafers were implanted a furnace curing (at 400 °C, 1 h, N_2 ambient) and followed by O_2-plasma treatment. Oxygen plasma was generated in a plasma-enhanced chemical vapor deposition chamber at a pressure of 400 mTorr with a radio frequency power of 200 W. The flow rate of oxygen gas was 500 sccm. After okay, Al electrodes were evaporated on the front surface of the films and backside of the substrate to complete the metal–insulator–semiconductor device. Infrared spectrometry was performed from 4000 to 400 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer calibrated to an unprocessed wafer, for determining the chemical structure of HSOP films after O_2 plasma treatment or X-ray exposure. Dielectric property measurements were conducted using a Keithley Model 82 CV analyzer. The area of gate electrode was 0.00528 cm^2 for $C-V$ analysis. The leakage current ($I-V$) characteristics of dielectric were measured using a HP4156 electrical meter. Finally, we used HOSP solution to dissolve the unexposed portion of the HOSP films, and observed the final pattern by scanning electron microscope (SEM) image.

3. Results and discussions

In the conventional damascene processes, PR removal is an inevitable step. The PR removal was carried out on selected wafers utilizing conventional O_2 plasma ashing. Therefore, the impact of O_2 plasma ashing on the quality of HOSP film was investigated in this study. Fig. 3 shows the FTIR spectra of HOSP film with and without O_2 plasma treatment. The intensity of Si–OH bond peak and H_2O increased after O_2 plasma ashing. Furthermore, the intensity of Si–H, C–H and Si–CH_3 peaks decreased dramatically. This indicated a moisture uptake appear increased after O_2 plasma ashing. Fig. 4 shows the leakage current density of furnace-cured HOSP film before and after O_2 plasma treatment. The leakage current increased approximately two orders magnitude after O_2 plasma treatment. Furthermore, the dielectric constant also increased greatly after O_2 plasma treatment, as shown in Fig. 5. The dielectric loss is due to the destruction of functional groups in the HOSP films after O_2 plasma ashing process, which is consistent with the FTIR spectra in Fig. 3.

In order to overcome these limitations, a novel patterning method using X-ray exposure is proposed to manufacture the damascene structure. Furthermore, in the deep sub-micron lithography technology, compared

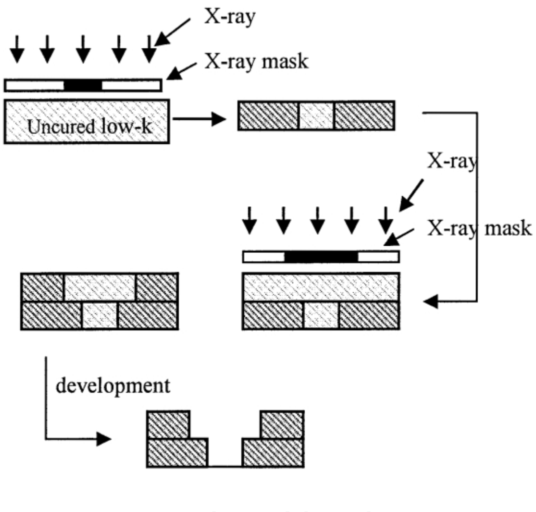

Fig. 2. Proposed X-ray lithography process.

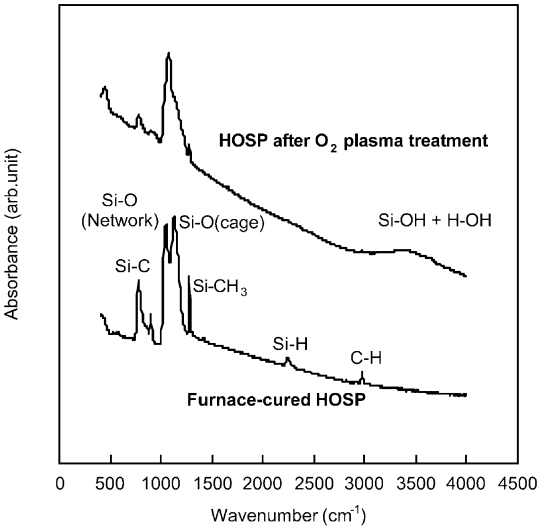

Fig. 3. FTIR spectra of HOSP films before and after O_2 plasma treatments.

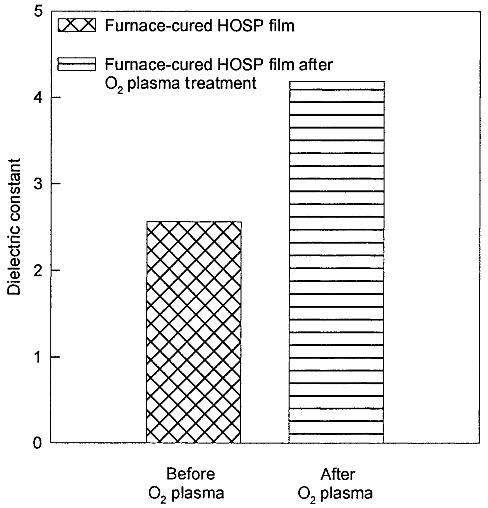

Fig. 5. Dielectric constants of as-cured HOSP films before and after O_2 plasma treatments.

with traditional deep UV lithography, the X-ray lithography technology has numerous advantages including higher resolution, higher intensity and shorter exposure times [11–16]. Therefore, the interaction of HOSP films and X-ray exposure is of great interest for the academic and industrial communities. Fig. 6 shows the FTIR spectra of HOSP films after X-ray exposure with different doses. The spectral results indicated that the chemical bonds of the bulk films have significantly changed after X-ray exposure. In the low dose regime, the spectra of HOSP films were almost the same as the as-baked film. With increasing the dose, the FTIR spectra of HOSP film changed gradually. The Si–O cage-like peak intensity at 1120 cm^{-1} became weaker, but the network-like peak intensity at 1043 cm^{-1} became stronger. This clearly shows that the material structure of HOSP changes from cage-like to network-like. Although, the peak intensity is not as strong as for the furnace-cured film, it is gradually becomes more similar to the furnace-cured film.

The leakage current density and dielectric constant of HOSP films after X-ray exposure were also evaluated. Fig. 7 shows the leakage current densities of X-ray exposed HOSP films at different doses. It is observed that the leakage current density of HOSP films distributed broadly among difference exposure doses. As a result of the magnitudes of leakage current density of X-ray exposed HOSP films at difference X-ray exposure

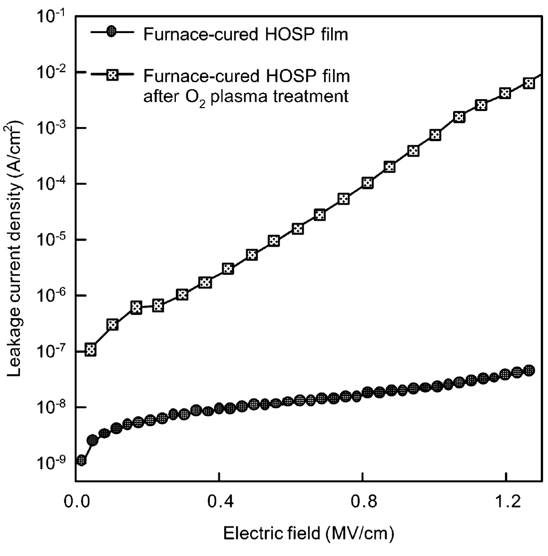

Fig. 4. Leakage current density of as-cured HOSP films before and after O_2 plasma treatments.

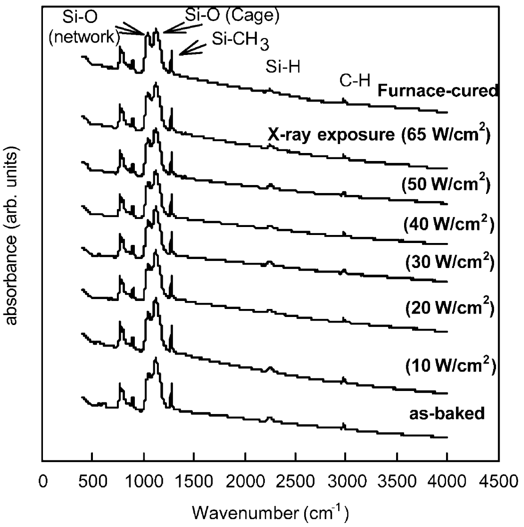

Fig. 6. FTIR spectra of HOSP films with different doses of X-ray exposure.

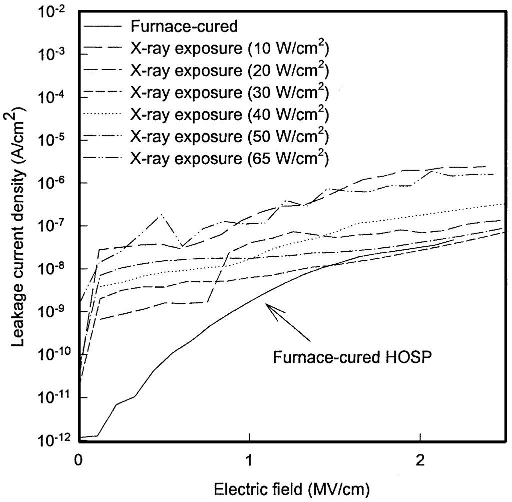

Fig. 7. The leakage current densities of X-ray exposed HOSP films at different doses without furnace annealing process.

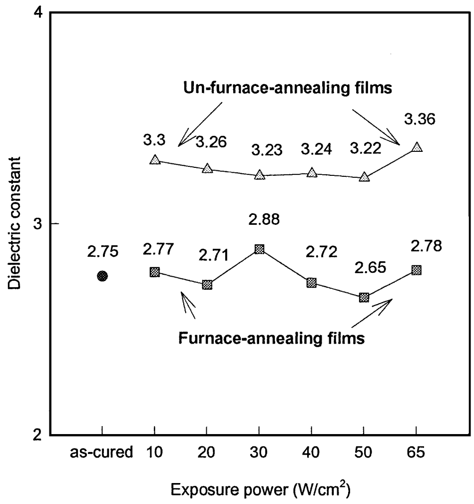

Fig. 9. The comparison of dielectric constants of X-ray exposed HOSP films at different doses with and without furnace annealing.

doses are all higher than that of furnace-cured film, thus we tried transferring these wafers to a furnace for further thermal annealing. Fig. 8 shows the leakage current densities of X-ray exposed HOSP films at different doses with an additional annealing in furnace at 400 °C for 1 h. It is observed that the leakage current densities are all significantly reduced after furnace annealing and are close to that of the furnace-cured HOSP at higher fields. Fig. 9 shows the comparison of dielectric constants of X-ray exposed HOSP films at different doses with and without furnace annealing. Although, the dielectric constants of HOSP films after X-ray exposure without furnace annealing are higher than that of the furnace-cured HOSP film, it is obvious that the dielectric constants of HOSP films after X-ray exposure with furnace annealing are lower and closer to the furnace-cured film. Therefore, the results point out that even though optimal electrical dielectric properties of HOSP film cannot be obtained directly by the X-ray curing process, we can utilize post-exposure furnace annealing process to recover the electrical dielectric characteristics.

Finally, a circle image with area of 5.03×10^{-5} cm^2 was formed by X-ray patterning to verify its practicability. In this study, we used the HOSP solvent to develop the pattern, and the result is shown in Fig. 10. An obvious image appears after X-ray patterning. In a word, X-ray direct exposure on the low-*k* HOSP can be extendedly used to fabricate Cu damascene structure. Additional study is required to perfect the patterning resolution, but it is likely this can be fine-tuned by varying the X-ray exposure time and dose. After the

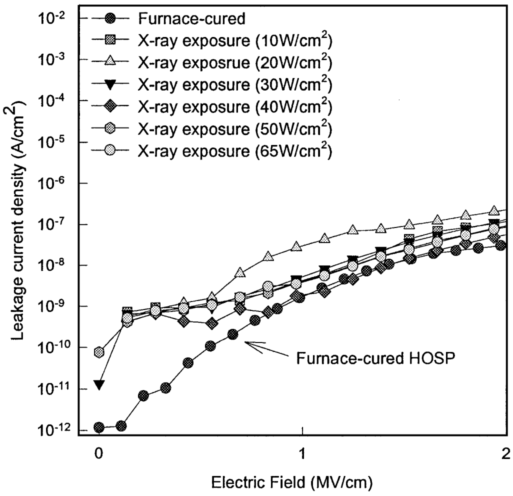

Fig. 8. The leakage current densities of X-ray exposed HOSP films at different doses with furnace annealing process.

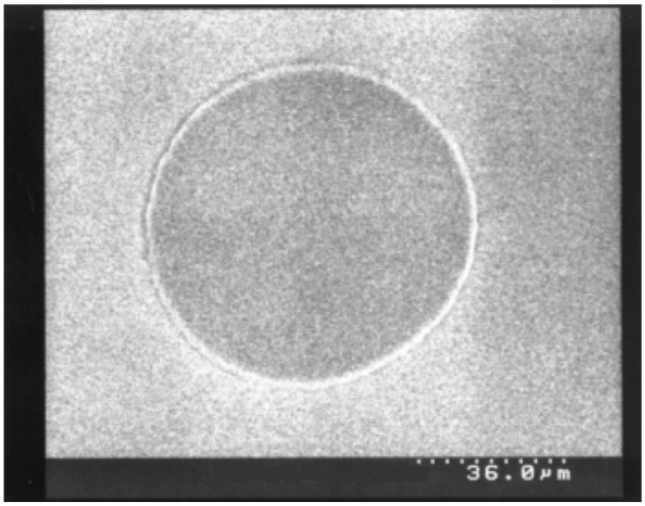

Fig. 10. The SEM image of patterned wafer after X-ray curing and development without post-exposure annealing. And its diameter dimension is 80 μm.

pattern is finished, the electrical dielectric characteristics of HOSP can be recovered by the post-exposure furnace annealing.

4. Conclusions

X-ray lithography for low-*k* HOSP as inter-metal dielectric has been investigated in this paper. Materials analysis and electrical properties show oxygen plasma tends to attack the Si–H and Si–CH_3 bonds in HOSP film during PR ashing process. The breaking of functional groups will speed up dielectric degradation and moisture absorption. This makes both leakage current and dielectric constant of HOSP film increase.

We proposed a novel X-ray direct patterning on the HOSP film to avoid the damage of PR removal process. The X-ray curing has been shown to effectively cure HOSP films to make the cage-like bonds of HOSP transform to network bonds. Then, the part of HOSP films without X-ray cured can be developed using the same HOSP solvent. In addition, the leakage current density and dielectric constant of HOSP films can be recovered by post-exposure furnace annealing. The method can be incorporated into next generation of multilevel interconnect systems as the devices shrink into nano-scale regimes.

Acknowledgments

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