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Interaction of Cu with low- k plasma polymer films deposited by PECVD using decahydronaphthalene and tetraethylorthosilicate precursors

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1. Introduction

Cu is an attractive material for interconnect metallization due to its low bulk resistivity and high reliability against electromigration. However, it tends to diffuse into the dielectrics, causing leakage currents. For this reason, diffusion barrier layers made of hard materials such as Ta, TaN and TiN are required. These barrier layers, however, have much higher resistances than Cu, which will increase the overall resistances of the metallization, especially for devices with small linewidths. It is considered that metallization without diffusion barriers can improve the semiconductor device performance significantly. Recently, Tada *et al.* reported that barrier-metal-free Cu dual-damascene interconnects reduced the via-resistance by 50 % [1]. For the barrier-metal-free metallization, low- k materials into which Cu does not diffuse within a proper range of manufacturing process window and/or operation condition will be required. Therefore, it will be important to investigate the interaction of Cu with low- k materials upon, for example, high temperature annealing.

In this work, effects of annealing on the properties of a structure made of Cu and low- k plasma polymer were investigated. Low- k plasma polymer films used in the experiment were deposited using a mixture of decahydronaphthalene ($C_{10}H_{18}$: DHN) and tetraethylorthosilicate ($Si-(O-C_2H_5)_4$: TEOS) as the precursors and were referred to as PPDHN:TEOS films. Deposition using a mixture of DHN and TEOS as the precursor was employed because, in our experiments, it was found that deposition using a mixture of DHN and TEOS produced thin films with both low k values and high thermal stability compared to that using DHN only or TEOS only [2]. In this report, films deposited from DHN and TEOS were referred to as PPDHN films and PPTEOS films, respectively.

2. Experiments

PPDHN:TEOS films were deposited by a PECVD system. The DHN and TEOS monomers were vaporized in the precursor bubbler kept at 75 °C and 30 °C, respectively. During the deposition, the pressure of the deposition chamber and the r.f. power density were kept at 0.5 torr and 0.38 W/cm², respectively. The films were deposited on silicon (p-Si(100)) substrates at room temperature. By

optimizing deposition conditions and post-deposition treatment conditions, PPDHN:TEOS thin films with k value of 2.7 could be produced and were used in this work. After Cu dots were deposited on the PPDHN:TEOS film by sputter, some of the Cu/PPDHN:TEOS/Si samples were annealed at 400, 450, 500, and 580 °C in Ar ambient of 0.3 torr for 30 min. We made Cu/PPDHN:TEOS/Si/Al structures for measurement of current-voltage (I-V) characteristics. Fourier transform infrared (FTIR) spectra were measured for PPDHN:TEOS films deposited on silicon substrates to investigate the chemical structures of the films. To investigate the Cu profile at the Cu/PPDHN:TEOS interface, time of flight secondary ion mass spectroscopy (TOF-SIMS) analysis was performed using a Cs⁺ beam.

3. Results and discussion

Figures 1(a), 1(b) and 1(c) show FTIR spectra of PPDHN, PPDHN:TEOS, and PPTEOS, respectively. For Figs. 1(a) and 1(c), the FTIR spectra were measured from as-deposited PPDHN and PPTEOS films. Fig. 1(b) can be thought as Figs.1(a) and 1(c) combined except OH and C=O groups, indicating that the PPDHN:TEOS film contains both DHN-related species and TEOS-related species in the film. The ratio of peak intensities of Si-O stretching and CH_x stretching, $I(Si-O)/I(CH_x)$, of Fig.1(b), 4.61, was about 4 times less than that of Fig. 1(c), 16.83. In addition, the PPTEOS film has peaks for CH_x at 2978, 2938 and 2902 cm⁻¹, which are thought to be from the TEOS precursor, while for the PPDHN:TEOS film, CH_x peaks at 2962, 2928, and 2862 cm⁻¹, which are from the DHN precursor [3], are notable. Above results indicate that PPDHN:TEOS has a significant amount of species from DHN and has much lower densities of Si-O groups than PPTEOS.

Figure 2 shows I-V characteristics of the Cu/PPDHN:TEOS/Si/Al structure, for which Cu/PPDHN:TEOS/Si was annealed at 400, 450, 500 and 580 °C in Ar ambient of 0.3 torr for 30 min before the Al back-contact deposition. 400 and 450 °C annealed samples did not show a increase of leakage current density compared to the not-annealed sample. Instead, the leakage current densities of the 400 and 450°C annealed samples were less than that of the not-annealed sample. It is thought that the defects at the poor interface between PPDHN:TEOS and Cu

of the not-annealed sample causes leakage current [4] and when the sample was annealed at high temperature, e.g., 400 or 450 °C, the interface improves and the leakage current reduces. The leakage current density of the 500 °C annealed sample, however, was higher than those of 400 °C and 450 °C annealed samples and was similar to that of the not-annealed sample. When the sample was annealed at 580 °C, remarkable increase of leakage current occurred. Figure 3 shows the Cu depth profile of the Cu/PPDHN:TEOS structure annealed at 450, 500, and 580 °C measured by SIMS. Before the SIMS analysis, the Cu film deposited on the PPDHN:TEOS films was removed by etching solution to avoid the matrix effect of Cu film. Cu depth profiles of the 500 °C and 580 °C annealed samples were similar to that of the 450 °C annealed sample, indicating that notable diffusion of Cu into PPDHN:TEOS film did not occur upon 500 °C or 580 °C annealing. From the data shown in Figs.2 and 3, it can be thought that the significant increase of leakage current upon 580 °C annealing for Cu/PPDHN:TEOS/Si/Al is due to the other changes of the samples than the diffusion of Cu into the PPDHN:TEOS film.

To investigate the change of structure of the PPDHN:TEOS film upon annealing, the FTIR absorption analysis was performed. Figure 4 shows change of the FTIR absorption spectra of PPDHN:TEOS films with the annealing temperature. The peak areas of CH_x stretching vibrations around 3200-2800 cm⁻¹ of the 500 °C and 580 °C annealed samples decreased by about 50 and 75 %, respectively, compared to that of the not-annealed, 400 °C and 450 °C annealed samples. In addition, for 500 °C and 580 °C annealed samples, the intensity of Si-H bending peak around 885 cm⁻¹ decreased notably. The decrease of CH_x peak and Si-H peak indicates that dissociation of carbon and hydrogen occurs. PPDHN:TEOS films with dissociated carbons and hydrogens are considered to have dangling bond generation and moisture absorption, which were reported to increase the leakage current in plasma polymers [5]. In addition to decrease of CH_x peak and Si-H peaks, Si-O peak shift was observed. For 500 °C and 580 °C annealed samples, the Si-O absorption peak shifted to lower wavelength, from 1072 cm⁻¹ to 1053 cm⁻¹.

4. Summary

We investigated the effects of annealing on the properties of a structure made of Cu and low dielectric constant (low-*k*) plasma polymer. 500 °C and 580 °C annealed samples showed slightly and significantly higher leakage currents, respectively, than 400 °C and 450 °C annealed samples. Secondary ion mass spectroscopy analysis and Fourier transform infrared absorption spectroscopy analysis suggested that the increase of leakage current of

Cu/PPDHN:TEOS/Si/Al structures after 500 °C and 580 °C annealing are caused by the compositional and structural change of PPDHN:TEOS films, rather than by the diffusion of Cu into the PPDHN:TEOS films. It is expected that our PPDHN:TEOS films, when put adjacent to Cu, can remain insulating even after manufacturing processes performed at temperatures as high as 500 °C.

Acknowledgments

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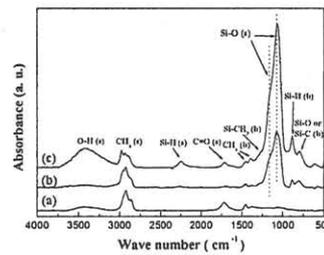


Fig. 1. FTIR spectra of the deposited films.

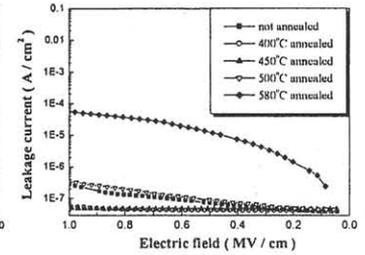


Fig. 2. I-V characteristics of Cu/PPDHN:TEOS/Si/Al structures.

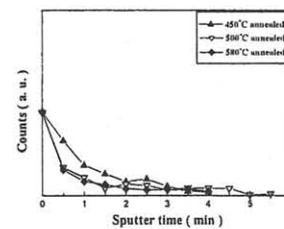


Fig. 3. Cu depth profiles of the annealed samples by SIMS.

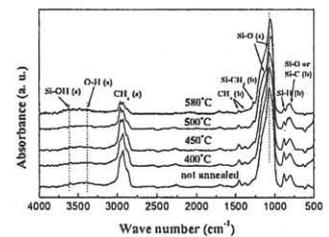


Fig. 4. FTIR spectra of the deposited films