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Comparative Measurements and Characteristics of Cu Diffusion into Low-Dielectric Constant para-xylene based Plasma Polymer Thin Films

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Abstract

Diffusion of Cu into the low-k para-xylene based plasma polymer (pXPP) thin films deposited by plasma-enhanced chemical vapor deposition using the para-xylene precursor was comparatively measured using various methods. Cu layer was deposited on the surfaces of pXPPs treated by N_2 plasma generated in a magnetically enhanced inductively coupled plasma reactor. Diffusion characteristics of Cu into pXPPs were measured using Rutherford backscattering spectroscopy (RBS), secondary ion mass spectroscopy (SIMS), cross-sectional transmission electron microscopy (XTEM), and current-voltage (I-V) measurements for the vacuum-annealed Cu/pXPPs for 1 hour at 450 ℃ and were compared. The results showed a correlation between the I-V measurement and SIMS data are correlated and have a sensitivity enough to evaluate the dielectric properties but the RBS or XTEM measurements are not sufficient to conclude the electrical properties of low-k dielectrics with Cu in the film bulk. The additional results indicate that the pXPP layers are quite resistant to Cu diffusion at the annealing temperature of 450 ℃ compared to the other previously reported organic low-*k* materials.

1. Introduction

Future integrated circuits demand the continuing shrinkage of device dimension in order to achieve high speed and performance[1, 2)]. RC (resistance-capacitance) delay increases with the shrinkage of device dimension and becomes the dominant limitation for device performance[3)]. New metallization process demands new conducting material with higher electrical conductivity and interlayer insulator with lower dielectric constant, in order to overcome the limitation of conventional Al and SiO_2 metallization scheme. Cu is very attractive for conductors due to its high electrical conductivity and electromigration resistance[4-6)]. Also, SiO_2 will be replaced by low-k materials owing to its high dielectric constant. Among various candidates for low-k materials, organic polymers are very promising because of their low dielectric constant[7)].

In this work, we used para-xylene based plasma polymer (pXPP) deposited by plasma-enhanced

chemical vapor deposition (PECVD) using the para-xylene precursor containing no fluorine (F) that causes various corrosion problems in interconnect[8]. Our previous work showed that these films have the dielectric constant as low as 2.70 and thermal stability up to 450℃[8]. And N_2 plasma treatment on the surface of pXPPs showed the generation of new functional groups that contribute to improvement in the adhesion between Cu and pXPPs[9]. The diffusion characteristics of Cu into the pXPPs as well as adhesion and thermal properties play very important roles in the interconnect performance.

Common techniques of measuring Cu concentration in the dielectric layers are X-ray photoelectron spectroscopy (XPS)[10], Rutherford backscattering spectroscopy (RBS)[11], cross-sectional transmission electron microscopy (XTEM)[12], secondary ion mass spectroscopy (SIMS)[11], and current-voltage (I-V) measurements[13]. Correlation between sensitivity ranges of various techniques for Cu detection and the electrical properties of low-k dielectric materials has not been evaluated in detail. In this study, we focus on the comparative measurements and diffusion characteristics of Cu into the bare and plasma-treated pXPPs by using RBS, SIMS, X-TEM, and the current-voltage (I-V) measurements for the vacuum-annealed Cu/pXPPs for 1 hour at 450 ℃. The results from the various measurements for the annealed samples with and without N_2 plasma treatments indicate the necessity of using very sensitive chemical measurements such as SIMS combined with electrical measurements in order to evaluate the effects of Cu diffusion on the properties of low-k dielectric materials.

2. Experimental procedure

pXPPs were deposited on silicon substrate by PECVD. The PECVD system used in this work is described elsewhere in detail[14]. The base pressure of the reactor equipped with a diffusion pump was $\cong 1\times10^{-6}$ Torr. Para-xylene as a precursor was contained in a bubbler heated at 40℃ and carried by Ar into the PECVD system. Plasma in the reactor was generated around the susceptor connected to an RF (13.56 MHz) generator. In this work, deposition of pXPPs was performed at 45℃ with Ar pressure of 2 Torr and RF power of 60 W for 30 min. The thickness of deposited pXPP films measured by α-step profilometer was $\cong$ 300 nm. For N_2 plasma surface treatment of pXPPs, a magnetically enhanced inductively coupled plasma (MEICP) equipment was used. Inductive power, the bias voltage, gas flow rate, and the plasma exposure time were 400 W, -50 V, 10 sccm, and 90 s for N_2 plasma surface treatment. The pressure during plasma treatments was maintained at 1×10^{-3} Torr.

After plasma treatments, Cu was deposited onto pXPPs by d.c. magnetron sputtering at room-temperature. The base pressure, Ar flow rate, and operation pressure during sputtering were 1×10^{-6} Torr, 10 sccm, and 5×10^{-3} Torr, respectively. The film thickness was fixed at 7 nm for XPS analyses. Deposition rates were calibrated by the thickness of Cu measured by RBS.

X-ray photoelectron spectroscopy (XPS) was performed using a model ESCALAB 220i-XL by VG. The spectrometer is equipped with a non-monochromatic Al K_α X-ray source generating photons with energy of 1486.6 eV. A neutralizer gun was used for the non-metal deposited sam-

ples to compensate for charging of polymer surface. For RBS measurements, the 2.0 MeV He^{2+} RBS probe beam was impinged on the sample at normal incidence and the detector was set at a scattering angle of 170°. The beam current of 20 nA was used to minimize the beam damage. XTEM observation was carried out using an electron microscope operating at an electron acceleration voltage of 300 keV. SIMS has been used to study the diffusion properties of Cu/pXPPs, using a Cameca IMS 4f. A Cs^+ primary ion beam having an impact energy of 14.5 keV and the beam current of 6nA was used for the SIMS depth profiling. For I-V measurement, ≅200-nm-thick Cu dots were sputter-deposited using shadow masks on the pXPPs formed on Si substrates. Some of Cu/pXPP/Si samples were annealed at 450°C. Al (200 nm) was deposited on the whole surface of the backside of the Si substrate. Cu dots of several sizes were used to ensure high accuracy of the I-V measurement.

3. Results and Discussion

In order to verify the effects of N_2 plasma treatment on the surface, XPS measurements of the untreated and plasma-treated pXPPs were carried out without any sputtering. The surface chemical composition of untreated pXPP consists of oxygen and carbon. In the case of N_2 plasma treatment, the C 1s and N 1s spectra showed the new binding states of C-N, C=N, or C=O-N functional groups were formed by the N_2 plasma treatment, as previously reported[9]. The adhesion strength of the Cu on pXPP surfaces was shown to be enhanced by additional binding states with Cu provided by new functional groups generated by plasma treatments compared to the adhesion property of Cu onto untreated surface of pXPP[9].

Figure 1 shows the RBS data for the as-deposited and annealed Cu/pXPP/Si samples. As seen in the spectra, no evidence of Cu diffusion into the pXPP layers can be observed from the Cu profiles within the detection limit of RBS. It is well known that atomic detection limit is a few atomic percent in RBS. These results show that Cu is much resistant to diffusion into pXPP layers compared to the previously reported cases that measured signal of Cu, indicative of significant diffusion of Cu, in the PI (polyimide) and parylene-N was detected by RBS at the annealing temperature of 350 and 400 ℃[11, 15]. For further measurement of Cu concentration in the pXPP layers, XTEM measurements were carried out. The XTEM micrographs in Figure 2(a), 2(b), and 2(c) are the cross-sectional images for the Cu/pXPP/Si sample with no thermal annealing, the Cu/pXPP/Si with thermal annealing, and Cu/N_2 plasmatreated pXPP / Si sample with thermal annealing, respectively. The thermal annealing was perfor-

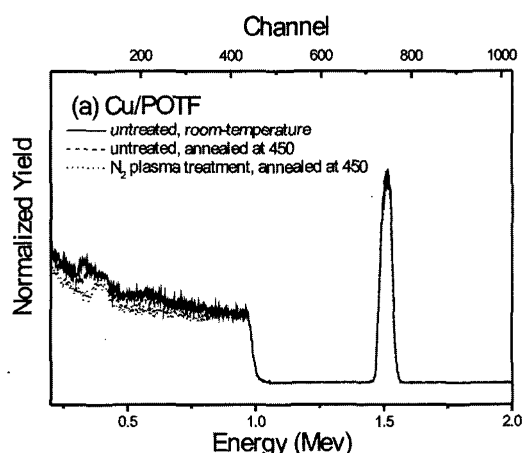

Fig. 1 RBS spectra measured before and after annealing at 450 ℃ for Cu (50 nm)/pXPPs

med in vacuum at 450 ℃ for 1 hour. Careful examinations of the micrographs did not show any indication of Cu agglomeration in the pXPP layers. The other reports show that Cu diffusion in the polymer layers results in the formation of Cu agglomerates in the bulk of polymer thin films[16]. It is worth while to mention the difficulty of sample preparation for TEM observation for the Cu/pXPP/Si sample with no thermal annealing because of extremely weak adhesion of Cu layer onto the surface of pXPP. As seen in Fig. 2 (c), the roughness of the interface between Cu and pXPP for the Cu/N_2 plasma-treated pXPP/Si sample with thermal annealing is larger than that of the Cu/pXPP/Si samples with and without thermal annealing. The increased adhesion[9] may be partly attributed to this increased surface roughening during plasma treatments in addition to the formation of new binding states for Cu atoms.

In order to further confirm any change in Cu profiles after thermal annealing, SIMS analyses were performed and the results are shown in Figure 3. All the signals were referenced to the C signal from the pXPPs. The dips near the interface of Cu/pXPPs are primarily caused by the charging effects of impacting ions due to the dielectric nature of pXPP layers. As seen in the results, Cu diffuses further into the pXPP layers for the annealed samples regardless of the N_2 plasma treatment of pXPP surfaces before Cu deposition. This observation of Cu diffusion into the low-k pXPP layers is the result of high sensitivity of SIMS measurements. It is well known that the SIMS detection limit for metals including Cu is about 10^{16} cm^{-3}.

In order to correlate the effects of Cu in the low-k pXPP layers on the electrical properties, I-V characteristics for the Cu/pXPPs were measured and the results are shown in Figure 4. The leakage current density values at -20 V with 0.4 MV/cm for the unannealed sample is as low as 10^{-7} A/cm^2. The leakage density values at -20V for the annealed samples dramatically increased from 10^{-7} to 10 A/cm^2. These results are presumably attributed to increased Cu concentration in the bulk pXPP due to Cu diffusion into pXPP layers during thermal annealing at 450 ℃. These electrical properties of the unannealed and annealed samples indicate the I-V measurements have sensitivity enough to evaluate the effects of Cu diffusion on the electrical properties of low-k

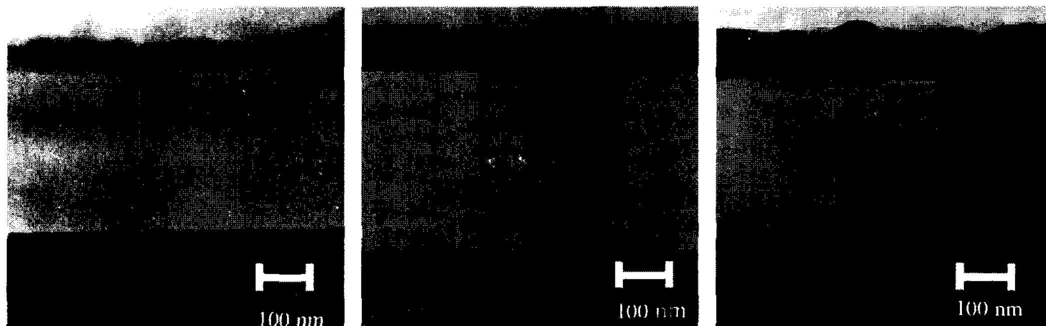

Fig. 2 Cross-sectional TEM images for (a) Cu/pXPP/Si without thermal annealing, (b) Cu/pXPP/Si annealed at 450°C, and (c) Cu/N_2 plasma-treated pXPP/Si annealed at 450°C.

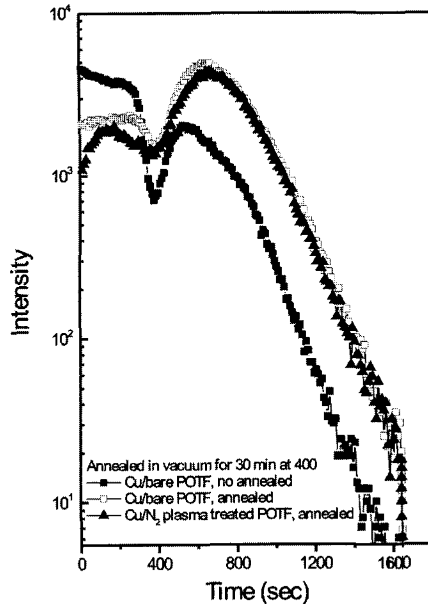

Fig. 3 Cu SIMS profiles measured before and after annealing at 450 ℃ for Cu ×100nm)/pXPP/Si

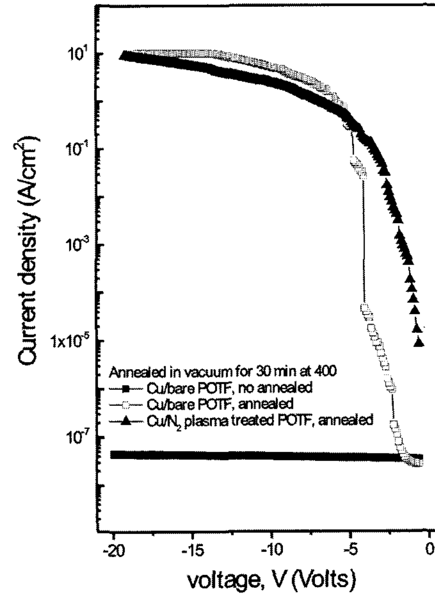

Fig. 4 I-V characteristics measured before and after annealing at 450 ℃ for Cu×100nm)/pXPP/Si

dielectric layers, together with SIMS measurements of Cu profiles.

Most of the previous measurements of Cu diffusion into the low-k organic dielectrics have been performed using the techniques with different Cu detection limits, including XPS, TEM, RBS, and SIMS[10-15]. Among those, as shown in the present experiment, SIMS has relatively high sensitivity comparable to the electrical measurements. For investigation of Cu diffusion effects on the electrical properties, a quantitative SIMS and I-V measurements is expected to give an insight into the role of Cu diffusion in the low-k dielectric layers. For detailed quantification of threshold chemical Cu concentration that causes abrupt increase in the leakage currents, quantitative analyses of Cu concentration in the intermetal dielectric materials using the techniques with high sensitivity for Cu detection are required.

Even though SIMS and I-V measurements show the diffusion of Cu into the pXPP layers at the annealing temperature of 450 ℃, the concentration of Cu was below the detection limit of RBS or TEM measurements. Compared to the present results, most previously reported results of other organic low-k dielectrics showed the concentration of Cu above detection limits of XPS, RBS or TEM at the annealing temperature range of 300 -350 ℃[11-15]. Observed higher resistance to the Cu diffusion, within the detection limit of RBS, XPS or TEM, is presumably attributed to the increased cross-liking resulting in the more dense films under the energetic particle bombardment on the pXPP surfaces during PECVD. Similar research results were observed in the Cu diffusion into the polyimide layers deposited by ionized cluster beam deposition with hyperthermal incident particles onto growing film surfaces[15].

4. Conclusion

In conclusion, it is very important to use the proper measurement techniques with high sensitivity in order to evaluate the electrical properties of low-*k* intermetal dielectric materials. Combining SIMS and I - V measurements can give an insight into the effects of Cu diffusion on the electricalproperties of low-*k* organic dielectric layers. In order to correlate the Cu chemical concentration and leakage current level in the low-*k* dielectric layers quantitatively, it needs a quantitative SIMS analyses combining with I-V measurements. The measurement results in the present study indicate that the pXPP layers are more resistant to Cu diffusion at the annealing temperature of 450 ℃ compared to the other previously reported organic low-*k* materials.

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