Chemical interaction, adhesion and diffusion properties at the interface of Cu and plasma-treated thiophene-based plasma polymer (ThioPP) films

K.J. Kim*a, N.-E. Leea, M.C. Kimb, J.-H. Booa

aDepartment of Materials Engineering and Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon, Kyunggi-do 440-746, South Korea
bDepartment of Chemistry, Institute of Basic Science, and Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon, Kyunggi-do 440-746, South Korea

Abstract

Chemical interaction, adhesion and diffusion properties at the interface of Cu and plasma-treated thiophene-based plasma polymer (ThioPP) films deposited by plasma-enhanced chemical vapor deposition (PECVD) were studied. Surface characterization of ThioPP films treated by Ar and O plasma using X-ray photoelectron spectroscopy (XPS), contact angle measurements, and atomic force microscopy (AFM) showed the formation of C=O chemical bonds by O plasma treatment and increase in surface roughness resulting in the decrease of contact angle. The chemical interaction between Cu and plasma-treated ThioPP films investigated by XPS showed the formation of Cu–S chemical bonding resulting in the strong adhesion of Cu on ThioPP films. Diffusion properties of Cu/ThioPP films annealed at 450°C for 1 h were surveyed by current–voltage (I–V) measurement. The slight reduction of Cu diffusion into ThioPP films treated by O2 plasma compared to that of the samples untreated or treated by Ar plasma is attributed to the formation of new chemical bonding states on the surface of O2 plasma-treated ThioPP films.

Keywords: Thiophene-based plasma polymer films; Plasma-enhanced chemical vapor deposition; X-Ray photoelectron spectroscopy

1. Introduction

Recently, there have been extensive research activities on the use of plasma for the polymerization of a number of organic and organometallic compounds. Plasma polymers can be used in many applications including interlayer dielectric materials, coatings for inhibiting corrosion, and low-friction surface coatings. Especially, with the integration density of semiconductor devices increasing, in order to decrease resistance–capacitance (RC) delay of integrated circuits, there has been increasing interest on Cu interconnect technology utilizing highly conductive Cu and low-k interlayer dielectric materials for the purpose of replacing the conventional Al and SiO2 metallization scheme [1–3]. Among the many candidates for low-k dielectric materials, organic polymers are very promising due to their low dielectric constant. However, Cu does not adhere well to organic dielectric materials and tends to diffuse into the dielectrics, which increases current leakage [4,5]. Glue and barrier metal layers such as Ta, Ti or their nitrides have been frequently used to improve adhesion of Cu and block Cu diffusion into intermetal dielectrics.

Thiophene-based plasma polymer (ThioPP) films used in the present experiments were synthesized using thiophene precursors activated and/or decomposed by plasma. Fig. 1 shows the chemical structure of thiophene precursor that consists of hydrogen, carbon and sulfur. ThioPP films were shown to have a dielectric constant as low as 2.70. The method of measuring the dielectric constant was described elsewhere in detail [6]. These films have an amorphous C–C cross-linked structure (including sp2-bonded and sp3-bonded carbon). It is reported that the C–C cross-linked structure maintains
the film’s thermal stability up to 450°C [7]. Also, these films have the advantage of containing no fluorine (F) that causes the various corrosion problems in interconnection [8].

Plasma polymer films often do not provide good interfacial adhesion to metals due to the absence of binding states between metals and plasma polymer. Our previous experiments on O₂ and N₂ plasma treatment of para-xylene-based plasma polymer (pXPP) films and cyclohexane-based plasma polymer (CHexPP) films showed the improvement in adhesion characteristics between Cu and pXPP [9], and CHexPP films [10]. Similarly, in order to activate surface and generate new functional groups that may contribute to improvement in adhesion between Cu and ThioPP films, we performed Ar and O₂ plasma treatment on the surface of ThioPP films. Also chemical interaction, adhesion, and diffusion properties at the interface between Cu and plasma-treated ThioPP films were investigated by X-ray photoelectron spectroscopy (XPS), contact angle measurements, atomic force microscopy (AFM), tape tests, and current–voltage (I–V) measurements.

2. Experiment

ThioPP films were deposited on Si substrate at an Ar and H₂ (2:1) mixture of gases at a pressure of 39.9 Pa by a radio frequency (r.f.) plasma enhanced chemical vapor deposition (PECVD) at 50°C. Before being loaded into the reactor, a p-type Si (100) substrate was cleaned in acetone, isopropyl alcohol, HF solution, and deionized (DI) water, sequentially. The base pressure of the reactor, pumped with a rotary pump, was less than 2.66 Pa. Thiophene (C₅H₇S) of the liquid phase, used as a precursor, was contained in a bubbler at room temperature. Ar (99.999% purity) and H₂ (2:1) mixture gases carried the thiophene into the deposition chamber. Plasma was generated around the substrate holder which is connected to a radio-frequency generator (50 W at 13.56 MHz).

After the deposition of ThioPP films, ex situ Ar and O₂ plasma treatments were performed on the films in an r.f. diode type reactor for 30 s and at room temperature. The applied r.f. power was 50 W. No bias was applied to the substrate holder. Cu was deposited onto the plasma-treated ThioPP films by d.c. magnetron sputtering of Cu (99.995% purity) targets. In order to minimize the damage of ThioPP film surfaces, the low d.c. power of 30 W was applied at the residual pressure of 0.532 Pa of Ar.

XPS measurements of the interface between Cu (5 nm) and plasma-treated ThioPP films were performed using a model MULTILAB ESCA 2000 by VG. The spectrometer is equipped with a non-monochromatic Mg Kα X-ray source generating photons with energy of 1253.6 eV. All analyses were performed at the pass energy of 20 eV and the energy step of 0.05 eV. Base pressure in the XPS analysis chamber was maintained at 3.99 × 10⁻⁷ Pa. A neutralizer gun was used for the non-metal samples to compensate for charging of polymer surface. All core level binding energies were referenced to the Cls signal at the binding energy, E₁s, of 284.6 eV. All spectra were taken at room temperature. For depth profiling, a 3.0-keV Ar⁺ sputtering was used.

The liquid probe used for contact angle measurements was DI water with a specific resistance of more than 18 MΩ/cm. The contact angle meter used was the Goniometer model 13-200-0 by ERMA. After pure water was dropped onto the surface of the plasma-treated ThioPP films, the contact angle of water on the films was immediately measured by means of the advanced angle method. All experiments were carried out at 25 ± 0.1°C.

Atomic force microscopy (AFM) was used in order to characterize the morphological change of plasma-treated ThioPP film surfaces. Images were obtained using a Nanoscope III by Digital Instruments with silicon nitride probes mounted on a cantilever. Imaging was performed in contact mode.

Adhesion strength of Cu (200 nm)/plasma-treated ThioPP films was assessed using a tape test. 3M Scotch™ Magic™ and 3M™ polyimide film tapes were used for the tape test. Some of the samples were annealed in vacuum at 450°C for 1 h in order to investigate any change of adhesion characteristics [10].

Diffusion of Cu into plasma-treated ThioPP films was characterized by current–voltage (I–V) measurement.
Fig. 2. C 1s core-level XPS spectra of plasma-treated ThioPP thin films. Fig. 2a showed the creation of the carbonyl group (C=O) at $E_s = 287.8$ eV.

Approximately 200-nm thick Cu dots were deposited on the plasma-treated ThioPP films by d.c. magnetron sputtering using a shadow mask. The diameter of Cu dots was 200 µm. Some of samples were annealed at 450°C for 1 h in vacuum to investigate the Cu diffusion properties.

3. Results and discussion

3.1. Surface properties of plasma-treated ThioPP films

Because plasma treatment can generate radicals and new functional groups on surfaces and/or can increase surface roughness, correlations between various surface properties need to be investigated. Characterization of surface chemical bonding states, relative surface energy, and surface morphology was carried out using XPS, contact angle measurements, and AFM, respectively.

Fig. 2 is the C 1s core-level XPS spectra obtained from the surface of plasma-treated ThioPP films. During the surface analyses, a 3.0-keV Ar+ sputtering was used for 120 s for each sample. The surface chemical species of untreated bare ThioPP films, determined from the spectra of Fig. 2c and Fig. 3d, consist of carbon (C), oxygen (O) and sulfur (S). The observed oxygen peak in Fig. 2c from the untreated bare ThioPP sample originates from the oxygen and H2O molecules adsorbed on the film surface in air because XPS measurements were performed ex situ following transportation of the samples in air. We could not perform the curve fitting of C–S and C–O separately in Fig. 2 because the binding energies of C–S (284.5–287.5 eV) and C–O (286.1–286.8 eV) are almost the same [11].

In the case of O2 plasma-treated ThioPP films, as shown in the C 1s spectra in Fig. 2a and in the O 1s spectra in Fig. 3c, a new chemical bonding state was observed at $E_b \approx 287.8$ eV corresponding to the binding energy of the C=O bond with a relatively small peak intensity. The chemical bonding states of S and O, however, were not found from the S 2p spectra of Fig. 4g.

Fig. 5 is a 2.0×2.0-µm AFM image of the surface of plasma-treated ThioPP films. The root-mean squared (RMS) roughness of untreated ThioPP films was 0.235 nm. However, the RMS roughness values of Ar or O2 plasma-treated ThioPP films were increased to 0.279 and 0.492 nm, respectively.
3.2. Interface formation of Cu/plasma-treated ThioPP films

Figs. 3, 4 and 7 are the O 1s, S 2p and Cu 2p$_{3/2}$ core-level XPS spectra of unannealed and thermally
annealed samples with and without plasma treatment. XPS analyses of the interface of Cu/plasma-treated ThioPP films were performed after sputtering the Cu layer to the point where the Cu/C composition ratio is approximately 0.4 using a 3.0-keV Ar+ ion sputtering, and the S 2p peak starts to appear. In the case of O2 plasma treatment, as seen in the O 1s spectra in Fig. 3a,b, the chemical bonding state which is considered to be O–Cu was created. The most significant peaks from the samples with Cu layers are ones corresponding to S–Cu with E_b = 162.4 eV, as seen in Fig. 4a–f. These peaks are quite strong from the samples with and without thermal annealing. O2 or Ar plasma treatments do not seem to affect the chemical bonding states between Cu and S on the ThioPP film surfaces. These peaks corresponding to S–Cu binding energy can be also confirmed from the Cu 2p3/4 spectra shown in Fig. 7. After thermal annealing of Cu/plasma-treated ThioPP films, any noticeable change in the chemical bonding states at the interface compared to those of samples without thermal annealing could not be observed. The results from the analyses of the XPS spectra in Figs. 4 and 7 indicate that the chemical interaction between Cu and ThioPP films occurs through the strong chemical bonding between Cu and S on the ThioPP film surfaces.

3.3. Adhesion properties

The adhesion properties were performed using a simple tape test. For this purpose, 3M Scotch™ Magic™ and 3M™ polyimide film tapes were used. The latter has a stronger adhesiveness on the Cu layer than the former. However, in the case of Cu/ThioPP films, all samples passed the tape test. As observed from the XPS spectra in Figs. 4 and 7, Cu–S chemical bonding states are presumably attributed to good adhesion properties in the present experiments. These results are contrary to the previously reported results that low-k polymer materials and plasma polymers require the modification of surfaces due to weak interfacial adhesion to metals [13,14]. Adhesion of Cu on ThioPP films is stronger than that of Cu on plasma polymers without sulfur on the surface [9,10].

3.4. Diffusion properties

Approximately 200-nm thick Cu dots were deposited on the plasma-treated 500–600-nm thick ThioPP films by d.c. magnetron sputtering using a shadow mask. Cu diffusion during thermal annealing was investigated by measuring leakage current density using the I–V method. The used voltage range was from –5 to 0 V. Fig. 8 shows the leakage current density values measured for different samples. Unannealed samples have a good electrical property, as determined from the result that leakage current density range is in the order of 10^-8 A/cm². However, all thermally annealed samples in vacuum at 450°C for 1 h showed a large increase in the leakage current density compared to that of the untreated samples. In the case of the thermally annealed samples, the leakage current density was high. These results indicate that Cu was significantly diffused into ThioPP films. However, for the thermally annealed O2 plasma-
treated samples, the leakage current density increased to the order of $10^{-5}$ A/cm$^2$ at $-5$ V which is smaller than those of the thermally annealed untreated or Ar plasma-treated samples. It is assumed that O$_2$ plasma treatment is slightly superior to Ar plasma treatment in terms of blocking Cu diffusion at $-5$ V. These results are consistent with the other experimental results by Du et al. [15] that oxygen plasma treatment is more effective compared to Ar plasma treatment in blocking Cu diffusion into low-$k$ organic dielectrics.

4. Summary

Chemical interaction, adhesion, and diffusion properties of Cu/plasma-treated thiophene-based plasma polymer (ThioPP) films were studied. Surface characterization of ThioPP films treated by Ar and O$_2$ plasma were performed by X-ray photoelectron spectroscopy (XPS), contact angle measurements, and atomic force microscopy (AFM). The results showed the formation of C=O bonds by O$_2$ plasma treatment and increase in the surface roughness of plasma-treated surface resulting in the decrease of contact angles. Analyses of XPS spectra from the interface between Cu and plasma-treated ThioPP films showed the peaks corresponding to the binding energy for Cu–S bonding. Observed strong adhesion of Cu on ThioPP films is presumably attributed to the formation of Cu–S chemical bonding states. Diffusion properties of Cu/ThioPP films annealed at $450^\circ$C for 1 h were surveyed by current–voltage ($I-V$) measurement. It was found that Cu diffusion into O$_2$ plasma-treated ThioPP films is smaller than that into untreated or Ar plasma-treated ThioPP films.

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References