Comparison of their electrical, optical, and electrochemical properties of as-grown plasma polymerized organic thin films by PECVD

I.-S. Bae \(a\), C.-K. Jung \(a\), S.-H. Jeong \(a\), S.-J. Cho \(a\), Y.J. Yu \(b\), J.G. Kim \(b\), J.-H. Boo \(a,\ast\)

\(a\) Department of Chemistry and Institute of Basic Science, Sungkyunkwan University, Suwon 440-746, Korea

\(b\) Department of Advanced Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea

Available online 20 January 2006

Abstract

Plasma polymerized organic thin films have been deposited on Si(100), glass and metal substrates at 25~100 °C using thiophene and toluene precursors by plasma enhanced CVD method. In order to compare physical and electrochemical properties of the as-grown thin films, the effect of the RF (13.56 MHz) plasma power in the range of 30~100 W and the deposition temperature on the corrosion protection efficiency and optical property were mainly studied in this work. Corrosion protection efficiency (\(P_k\)), which is one of important factors for corrosion protection in the interlayer dielectrics of microelectronic devices application, provided an increasing tendency with increasing RF power. The highest \(P_k\) value of plasma polymerized toluene film (85.27% at 70 W) was higher than that of the plasma polymerized thiophene film (65.17% at 100 W). The result of contact angle measurement showed that the plasma polymerized toluene films have more hydrophobicity than that of the plasma polymerized thiophene films.

1. Introduction

As the critical dimension of integrated circuits (IC) is scaled down, the line-width and spacings between metal interconnection are made smaller. New materials must be introduced into IC fabrication. The use of advanced inter-metal dielectrics to reduce the capacitance seems to be more important than the decrease of the resistivity provided by the substitution of aluminum by copper [1]. The reason is that the capacitance affects the device in three ways. The clock speed can be increased due to lower signal delay time of interconnects in ultra large scale integrated circuits (ULSI), cross-talk will be reduced between parallel lines and the power dissipation can also be decreased.

To lower the propagation delay, the most important issue will be how to lower the dielectric constants (\(k \leq 3.0\)) of interlayer dielectrics rather than lowering the resistance of interconnect metals [2,3]. High thermal stability as well as low dielectric constant is also an important requirement for the interlayer dielectrics. Therefore, polymerized thin films are now being studied intensively as the low \(k\) value and high thermal stability [4]. Plasma polymerized thin films can be formed easily by PECVD method. Properties of plasma polymerized thin films were related to deposition conditions such as the plasma power [5,6] and the substrate temperature [7]. Moreover, improved corrosion protection in the interlayer dielectrics is also required for the new generation of microelectronic devices.

In this study, we report primarily results on the growth of polymer-like organic thin films on glass, copper and silicon substrates at the deposition temperature in the range of 25 to 100 °C and various RF power using the thiophene and toluene precursors by PECVD method.

The body of this paper will be focus on performing analysis of electrical and electrochemical properties of plasma polymerized organic thin films.

2. Experiment

Plasma polymerization depositions are carried out in a stainless steel vacuum chamber. The steel and copper metals were used as both substrates and electrodes for electrochemical
measurements. Si(100) and glass substrates were used for low dielectric and optical property measurements. After cleaning the samples with acetone, isopropyl alcohol and distilled water, the substrates were pre-treated with Ar plasma in the vacuum chamber to enhance film adhesion. The typical conditions of the PECVD process used in this study for film deposition were 30-100 W of RF (13.56 MHz) power, 20 sccm of Ar carrier gas, and 20 sccm of H2 bubbler gas. The details of the experimental procedure have already been reported in the previous papers [8,9]. The typical deposition pressure and temperature were 2-4 × 10^{-1} Torr and RT (25 °C) to 100 °C. Thiophene (C4H4S) and toluene (C7H8) were used as organic precursors. Due to the high vapor pressure of the precursors themselves, it was not necessary to heat the source during deposition.

An impedance analyzer was used for the determination of the I−V curve for leakage current density and C−V curve for dielectric constants, respectively. Polarization measurements of the electrodes, both bare and covered with thiophene and toluene films were carried out potentiodynamically in 3.5 wt.% NaCl-solution at room temperature. The surface and optical properties of as-grown plasma polymerized thin films were analyzed by contact angle measurements, X-ray photoelectron spectroscopy (XPS), and Fourier transform IR spectroscopy (FT-IR).

3. Results and discussion

To determine surface composition, the films were analyzed with XPS first. Fig. 1a shows the X-ray photoelectron spectra of the polymerized thin films deposited at 100 °C and 100 W of RF power with Ar:H2=1:1. The spectrum obtained without Ar+ ion sputtering clearly shows the photoelectron peaks of S 2s, S 2p, and C 1s and C (KVV) Auger signal as well as O 1s and O (KVV) Auger transition. After sputtering for 1 min or even more, however, we did not detect any oxygen species through the film layers, signifying the formation of an oxygen free polymerized thin film. This indicates that the oxygen layer exists only on the surface films because of no further oxygen contamination of the newly formed film which resulted from exposure to atmosphere. The composition ratio of carbon and sulfur in the film was varied from 6:1 to 8:1 with increasing RF power to 100 W under the deposition condition of Ar:H2=1:1. We expect that the carbon contents influence the corrosion protection effectualness of thin film.

Fig. 1b shows FT-IR spectra of thiophene monomer and as-grown thin films deposited at 100 °C and Ar:H2=1:1 with different RF powers. The absorption peak at 2910 cm−1 can be assigned to the aliphatic C−H stretching mode by methyl and/or methylene groups. The threefold C−C bond of a fragment from the thiophene ring can be found at 2200 cm−1. This means that a considerable amount of monomer fragmentation takes place during the plasma polymerization. Thus, the plasma polymerized thin films with thiophene precursor can exist as a mixture of dimer, trimer, etc. This is in good agreement with the XPS results. The C=C structure may also be originated from the mesh structure of the thin film which is usually observed in the plasma polymerized films. In addition, we could see the increase of absorption peak intensities whenever the polymerization was carried out at high RF power. This indicates that more high quality films can be deposited using high RF power, reflecting more high protection efficiency.

Fig. 2a shows the change in the dielectric constants obtained from experimentally observed C−V curves using the MIM structure as a function of RF powers. Fig. 2b also shows the leakage current densities for the thiophene thin films that were grown at 100 °C and various RF powers with Ar:H2=1:1. With increasing the RF powers, the obtained dielectric constants decreased from 3.51 to 3.22. From the Fig. 2b, we determined the insulating properties of the films by measuring the leakage current density (J) with different applied fields (F). As the plasma power increases from 50 to 100 W, the leakage current densities decreased and the breakdown did not occur below 1 MV. This indicates that the films have a compact structure with high density and pin-holes free, which lowers leakage current density and increases breakdown field. The best leakage current density at RF power of 100 W was measured to be about 10^{-11} A/cm² at 1 MV/cm, suggesting that this polymer-like thin film can be used as insulating material and corrosion protection layer for microelectronic devices.
To determine other electrochemical properties of the polymerized organic thin films, we also studied on the corrosion protection efficiency. Fig. 3a shows polarization curves of the electrode, both bare and covered with thiopene film that grew on a steel plate at 100°C, 100 W RF power and Ar:H₂ = 1:1. In the Fig. 3a, we know that corrosion protection is enhanced with increasing RF power. To understand this phenomenon in detail, we also measured contact angle measurements (see Fig. 3c). The values of contact angles are increased from 66.8° to 80.8° with increasing RF power to 100 W, which indicates that the plasma-polymerized thiophene film will have high hydrophobicity and low surface energy with increasing RF power. With the results of XPS, FT-IR, and contact angle measurements, therefore, the following conclusions could be drawn on the basis of the above discussion. The plasma-polymerized thiophene film in 3.5 wt.% NaCl-solution provided an increased corrosion performance with increasing RF power. The crystal quality, contact angles, carbon contents, surface roughness are increased with RF powers while the dielectric constants and leakage current density are decreased. This is suggesting that the ability of corrosion protection in the interlayer dielectrics will be affected by several factors, especially crystal quality, and film composition ratio. Fig. 3b shows the protective efficiency of plasma-polymerized thiophene film on steel disk as a function of RF power. The protective abilities increase with increasing RF power and the highest $P_k$ value was 65.17% at 100 W.

From the results of the electrochemical and electrical properties for the thiophene films, we realized that the corrosion protective efficiency can enhance with lowering dielectric constants and leakage current density of thiophene films. To test these things systematically, we did a plasma
polymerization with toluene precursor that contains no sulfur while expecting more good corrosion protective ability.

For comparative study, therefore, we have deposited plasma polymerized organic thin films using toluene precursor under the same deposition condition of the thiophene films, and studied again their corrosion protection efficiency. Fig. 4a shows potentiodynamic curves of the copper disk covered with toluene films as a function of RF power and deposition temperature. In Fig. 4b, the protective abilities of films increased with increasing RF power and deposition temperature. The highest protective efficiency was 85.27% for the film grown at 100 °C and 70 W. Also the electrochemical results show that the highest $P_k$ value of plasma polymerized toluene film (85.27% at 70 W) was higher than that of the plasma polymerized thiophene film (65.17% at 100 W), indicating inhibition of oxygen reduction because the densely packed and tightly interconnected toluene film acted as an efficient barrier layer to the diffusion of molecular oxygen. The contact angles of the plasma polymerized organic thin films are also increased with increasing RF power.

**Acknowledgments**

Support of this research by the Ministry of Commerce, Industry, and Energy in Korea is gratefully acknowledged. This work was also supported by the BK21 project of the Ministry of Education, Korea and by the Center for Advanced Plasma Surface Technology at the Sungkyunkwan University.

**References**