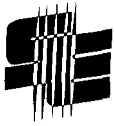

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Polymerized Organic Thin Films and Comparison on their Physical and Electrochemical Properties

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Abstract

Plasma polymerized organic thin films were deposited on Si(100), glass and metal substrates at 25~100 ℃ using thiophene and toluene precursors by PECVD method. In order to compare physical and electrochemical properties of the as-grown thin films, the effects of the RF plasma power in the range of 30~100 W and deposition temperature on both corrosion protection efficiency and physical properties were studied. We found that the corrosion protection efficiency (P_k), which is one of the important factors for corrosion protection in the interlayer dielectrics of microelectronic devices application, was increased 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), indicating inhibition of oxygen reduction. The densely packed and tightly interconnected toluene film could act as an efficient barrier layer to the diffusion of molecular oxygen. The result of contact angle measurement showed that the plasma polymerized toluene films have more hydrophobic surface than those of the plasma polymerized thiophene films.

Keywords : Organic polymer film, PECVD, Corrosion protection ability, Plasma polymerization

1. INTRODUCTION

There has been an increase of interest in the use of glow discharge for the polymerization of a number of organic and organometallic compounds. Plasma polymers are used as dielectric and optical coating to inhibit corrosion[1,2]. The investigation of the optical properties of polymer films is of particular interest because of their use in optical devices[1]. Moreover, with increasing integration density of semiconductor devices, multilevel metallization technology is even more important than it used to be[3]. Plasma-polymerized thin films as interlayer dielectrics have a high tendency to adsorb water in the presence of moisture and can act as an electrolyte. This situation results in galvanic corrosion between metallized conducting lines and electromigration (EM) under humid conditions. To prevent the multilevel interconnections effectively from corrosion-induced malfunction, it is necessary to examine corrosion problem resulting from a new-developed interlayer dielectric in microelectronic devices. In advanced logic devices with quarter micron design rules, the number of interlayer dielectrics has in-

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creased to four or five times, so that wiring delays are beginning to dominate the total signal delay in ultra large scale integrated circuits (ULSI). 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[3,4]. High thermal stability as well as low dielectric constant is also important requirements for the interlayer dielectrics. Moreover, improved corrosion protection in the interlayer dielectrics is also required for the new generation of microelectronic devices.

In this study, we report our primarily results on the growth of polymer-like thin films on glass, metal and silicon substrates in the deposition temperature range of 25 to 100℃ using thiophene and toluene precursors by PECVD method for semiconductor and optical devices applications.

2. EXPERIMENT

Plasma polymerization was carried out in a stainless steel vacuum chamber. The steel and copper metals were used as substrates and electrodes for electrochemical measurements. Si (100) and glass substrates were also used for optical property measurements. After cleaning the samples with acetone, isopropyl alcohol and distilled water, the substrates were in-situ pretreated with Ar plasma enhance film adhesion. The typical conditions of the PECVD process used in this study for the polymerized film deposition were 30~100 W of RF power, 20 sccm of Ar carrier gas, and 20 sccm of H_2 bubbler gas. The details of the experimental procedure have already been reported in the previous papers[5,6]. The typical deposition pressure and temperature were $2 \sim 4 \times 10^{-1}$ Torr and 25℃ to 100℃. Thiophene (C_4H_4S) and toluene (C_7H_8) were used as organic precursors. Due to the high vapor pressure of the precursors itself, it was not necessary to heat the precursors during deposition.

Firstly, in order to understand corrosion behavior of steel, we have measured potentiodynamic curve of steel in 3.5wt.% NaCl solution. Based on an electrochemical analysis, we could obtain the corrosion protection efficiency (P_k). Generally, the protective efficiency (P_k) of polymer coating can be defined as follows[7-9]:

$$P_k(\%) = 100\,(1 - K_f/K^0_f)$$

Where K_f and K^0_f represent the faradaic conductances (the reciprocal of the charge-transfer resistance) in the presence and absence of coating, respectively.

The surface property of as-grown plasma polymerized thin films was analyzed by contact angle measurements, X-ray photoelectron spectroscopy (XPS).

3. RESULTS AND DISCUSSION

To determine electrochemical properties of the thiophene thin films, we studied the corrosion protection effectiveness. Figures 1a shows polarization curves of the steel electrodes, both bare and covered with thiophene films. The cathodic branch of the polarization curves was markedly suppressed by coverage of the steel electrodes with the films. The anodic process was also inhibited in the presence of the film,

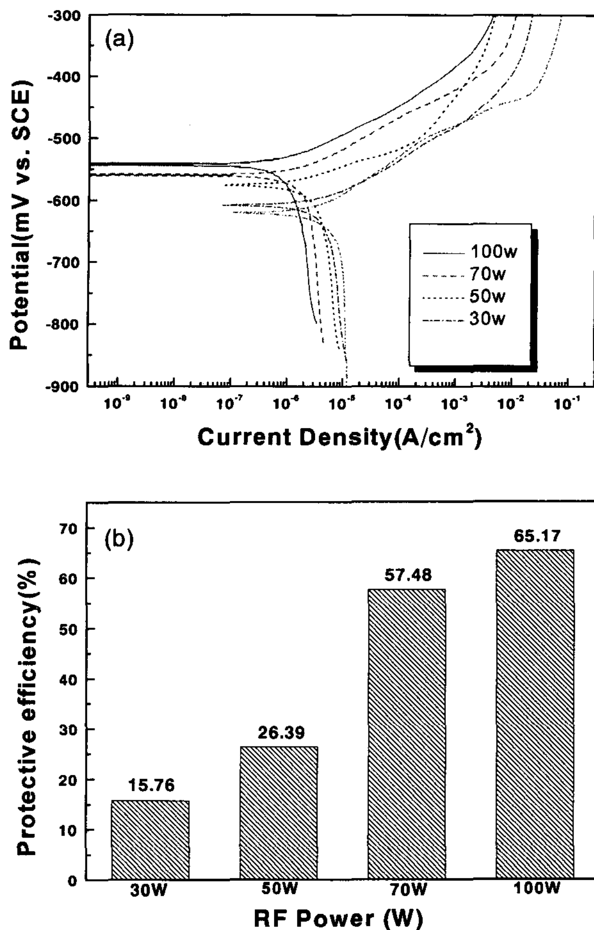

Fig. 1. Polarization curves and protective efficiency of a bare steel electrode and covered with thiophene film as a function of RF power; (a) Polarization curves and (b) protective efficiency.

suggesting that the tightly interconnected film suppressed diffusion of an electrolyte, like chloride ions, to the surface. From the figure 1a, we see that corrosion protection property is enhanced with increased RF power. Figures 1b shows the protective effectiveness of plasma-polymerized thiophene films on the steel disks as a function of RF power. The protective qualities increase with increasing RF power and show the highest P_k value of 65.17% at 100 W. The values of contact angles not shown were also increased from 66.8° to 80.8°° with increasing RF power to 100 W, which indicates that the plasma-polymerized thiophene film has high hydrophobicity and low surface energy with increasing RF power.

To determine surface composition, the as-grown films were also analyzed with XPS. Figure 2 shows the x-ray photoelectron survey spectra of a polymerized thin film deposited at 25℃ and 100 W of RF power with $Ar:H_2=1:1$. The spectrum obtained without Ar^+ ion sputtering clearly shows the photoelectron peaks of S_{2p}, S_{2p}, and C_{1s} and C(KVV) Auger signal as well as O1s and O(KVV) Auger transition. After Ar^+ ion 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 films surface because of no further oxygen contamination 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 from 30 W under the same deposition condition of $Ar:H_2=$

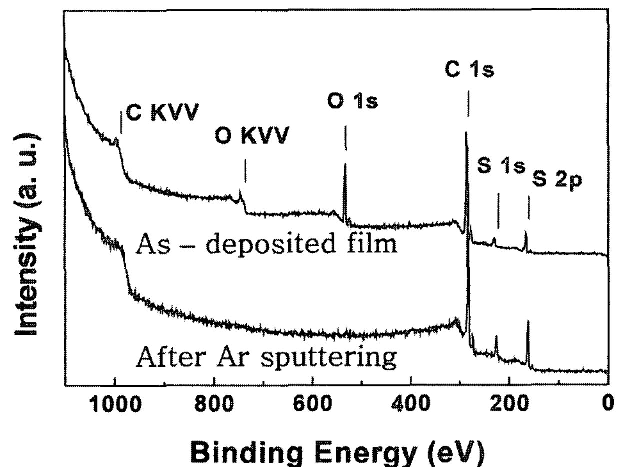

Fig. 2. XPS survey spectra obtained before and after sputtering for a film that grown at 100℃ and RF power of 100 W.

Table 1. Atomc composition of C and S obtained from thiophene thin films

	RF	C%	S%	O%
Before sputtering	50	49.5	15.0	35.5
	70	56.3	13.1	30.6
	100	71.0	9.4	19.6
After sputtering	50	76.7	23.3	0
	70	86.6	13.4	0
	100	88.6	11.4	0

1:1. In addition to the RF power effect, the composition ratio is also affected by the gas ratio. The carbon content of the film increased with higher Ar/H_2 ratio, due to Ar^+ ion sputtering effect and/or different sputtering yield. This indicates that structure of the as-grown films can be different from monomer structure. Table 1 shows the variation of composition of C and S obtained from the plasma polymerized thiophene thin films with RF power. It shows that the concentration of carbon in the film increases with increasing RF power. We expect that the carbon contents influenced the corrosion protection effectiveness of thin film. From the results of the electrochemical and surface properties of the thiophene films, we determined that high carbon content, and contact angles increased with RF power, and provided the good corrosion protection.

To comparative study, in this work, we deposited a organic polymer thin film using a toluene precursor under the same deposition condition as used for the growth of the thiophen film, and determined the corrosion protection. Figures 3a and 3b show potentiodynamic curves of copper disks coated with toluene films as a function of RF power and deposition temperature. The protective effectiveness of films increased with increasing RF power and deposition temperature.

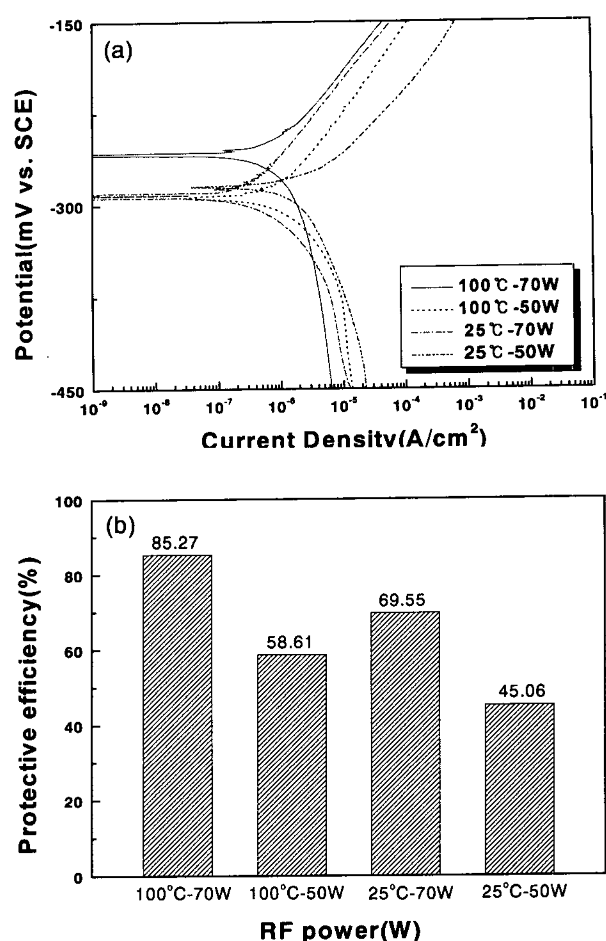

Fig. 3. (a) Polarization curves and protective efficiency of copper electrode covered with toluene films as a function of RF power and deposition temperature; (a) Polarization curves and (b) protective efficiency.

The highest protective effectiveness was 85.27 % at 100℃ - 70 W. Also these results show that the highest P_k value of plasma polymerized toluene film was higher than that of the plasma polymerized thiophene film (65.17% at 100 W). This means that the toluene film can inhibit the oxygen reduction rather than the thiophene film. The densely packed and tightly interconnected toluene film could act as an efficient barrier layer to the diffusion of molecular oxygen. The value of contact angle was enough to verify that the protective efficiency of toluene thin film was higher than thiophene thin film. In the case of toluene film deposition, nearly

same tendency of contact angle variation as thiophene films was obtained with RF power and deposition temperature. The contact angle of toluene thin film grown at 100℃ - 70 W was 85.3°. This indicated that the maximum contact angle of a toluene film (85.3°) grown at 70 W is larger them that of thiophene film (80.8°) grown at 100 W, indicating that relatively high dense film with more hydrophobicity can be obtained from the toluene film rather than thiophene film. The protective efficiency of plasma polymerized toluene film was higher than that of the plasma polymerized thiophene film.

4. CONCUSIONS

Polymer-like organic thin films were deposited at temperature in the range of 25℃ to 100℃ using the organic precursors such as thiophene and toluene monomers by PECVD method. To compare the electrochemical properties of the organic films, the effects of the RF plasma power and deposition temperature were investigated in this study. Corrosion protection efficiency (P_k) examined by potentiodynamic curve measurements in 3.5 wt.% NaCl-solution increased with increasing RF power and deposition temperature. 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). Contact angles are also increased with increasing RF power, indicating more hydrophobic surface formation.

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