Physical and optical properties of plasma polymerized thin films deposited by PECVD method


Abstract

Polymer-like organic thin films were deposited at room temperature and different radio-frequency (r.f.) powers by PECVD method using ethylcyclohexane as precursor. To compare the optical properties as well as the electrochemical properties of the organic films, the effects of the r.f. plasma power were mainly investigated in this study. The optical properties of as-grown plasma polymerized thin films were analyzed by ellipsometry and UV–visible spectroscopy. The corrosion protective abilities were also examined by potentiodynamic curves measurements in 3.5 wt.% NaCl solution. The experimental results show an increased of corrosion protective abilities for ethylcyclohexane were provided an increased corrosion performance with increasing r.f. power. The AFM and SEM data showed that the polymer films with smooth surface and sharp interface could be grown under different r.f. powers.

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

1. Introduction

Plasma polymers are used as dielectric and optical coating to inhibit corrosion. The investigation of the optical properties of polymer films is in particular interest because of their use in optical devices [1–4]. Plasma polymerization is a versatile technique for the deposition of films with functional properties suitable for a wide range of modern applications. This is due to the high degree of control of their properties, which may be varied widely by plasma parameters. Plasma polymerization is also known as a unique method of organic thin film deposition. The films are usually highly cross-linked polymers and show chemically and physically stable characteristics. However, the molecular structures of the films are different from starting monomers, because the polymers are formed with highly fragmented molecules under ions and electron collisions with high energy. That means PECVD uses a glow discharge to create activated species such as radicals and ions from the original monomer, and the polymer films are deposited through various gas phase and surface reactions of these active species, including ablation and irradiation with short-wavelength UV of the deposited film.

In this study, the deposition of plasma polymerized organic thin films on glass, Cu, and Si(100) substrates at room temperature using the ethylcyclohexane precursor by the PECVD method. The body of this paper will be focused on performing analysis of physical and optical properties of plasma polymerized organic thin films.

2. Experimental

Plasma polymerization was carried out in a vacuum chamber, which was made of stainless steel. The copper metal was used as the substrate as well as the electrode for study of electrochemical property (i.e. corrosion protection efficiency) while Si(100) and glass substrates were adapted for analysis of physical and optical properties of the as-grown films. After cleaning the samples using acetone, isopropyl alcohol and distilled water under the atmospheric condition, the pre-cleaned substrates have then been introduced into vacuum chamber immediately. After evacuating the chamber, the samples were in situ treated with Ar plasma to make a buffer
layer for enhancing film adhesion. The typical conditions of the PECVD process applied in this study for film deposition are 20–50 W of r.f. power and 20 sccm of Ar carrier gas, and 20 sccm of H₂ bubbler gas. The general deposition pressure and temperature were 26.66–53.33 Pa and room temperature, respectively. Ethylcyclohexane was used as organic precursor. Due to the high vapor pressure of the precursors itself, it was not necessary to heat the source during deposition.

Using copper electrodes both bare and covered with ethylcyclohexane, polarization measurements were carried out potentiodynamically in 3.5 wt.% NaCl solution at room temperature. The surface and optical properties of the as-grown plasma polymerized thin films were also analyzed with UV–visible spectroscopy, Ellipsometry, AFM, SEM and contact angle measurements.

3. Results and discussion

Fig. 1a shows the polarization curves of the Cu electrodes, both bare and covered with ethylcyclohexane films. Firstly, in order to understand the corrosion behavior of copper, potentiodynamic curve of copper in 3.5 wt.% NaCl solution was obtained. The cathodic branch of the polarization curves was markedly suppressed by coverage of the Cu electrodes with the films. The anodic process was also inhibited in the presence of the film, suggesting that the tightly interconnected film suppressed diffusion of an electrolyte, like chloride ions, to the surface. Fig. 1a also shows that the corrosion protection property is enhanced with increasing r.f. power. Fig. 1b shows the change of protective efficiency of the plasma-polymerized ethylcyclohexane films grown on copper substrates with different r.f. power. Generally, the protective efficiency ($P_k$) of polymer coating can be defined as follows [5–7]:

$$P_k(\%) = 100\left(1 - \frac{K_f}{K_f^0}\right)$$

where $K_f$ and $K_f^0$ represent the Faraday conductances (the reciprocal of the charge-transfer resistance) in the presence and absence of coating, respectively. The protective abilities increase with increasing r.f. power and the highest $P_k$ value was 92.1% at 50 W. This result shows that the protective abilities of ethylcyclohexane thin film are much better than polythiophene thin film under the same experimental condition [8]. To understand this phenomenon in detail, UV–visible spectra and contact angle measurements were recorded.

Fig. 2a shows UV–visible transmittance spectra of the plasma polymerized thin films that grew at room temperature under the condition of Ar/H₂ = 1:1 at different r.f. powers. From the figures for all organic thin films, a change of optical transmittance can be seen in the range of 300–350 nm (see inset) with a sharp slope and a high value of constant transmittance (~85%) through UV and visible regions. The remarkable fact is that the transmittance of films has a decreasing tendency with increasing r.f. power. Moreover, optical band gap was also decreased with increasing r.f. power. The reason for the blue shift tendency in the UV–visible spectra is mainly due to the higher degree of C=C double bonds in layers. This suggests that ethylcyclohexane films have a higher degree of cross-linking and C=C bonding with increasing r.f. power, because ethylcyclohexane molecule produces more radical sites with increasing r.f. power. Fig. 2b represents the variation of contact angles of glass substrates covered with ethylcyclohexane film as a function of r.f. power. The values of contact angles are also increased from 63.2° to 82.9° with increasing r.f. power to 50 W, which indicates that the plasma-polymerized ethylcyclohexane films will have high hydrophobicity and low surface energy with increasing r.f. power. Most notable is the fact that the surface roughness and post-deposition oxidation of the film surface would be affected by the contact angle. However,
the degree of cross-linking and/or number of fragmented radicals can be more important factors towards increasing the contact angles. Because the contact angle is decreased with increasing surface roughness and oxygen content, existing C=O or C–O bond related species.

Fig. 3a shows the change of film growth rate as a function of r.f. power. It shows that when the r.f. power was increased, the deposition rate was increased at room temperature. The nearly increasing of the deposition rate vs. r.f. power (see Fig. 3a) confirms the proposed mechanism of polymerization [9]: with increasing r.f. power the number of reactive fragments and atoms increases to form a random structured plasma polymer. Increases in the deposition rate with increasing r.f. power can thus be simply explained in terms of the increase of plasma density with an adequate amount of energy that can be used for plasma polymerization of ethylcyclohexane precursor. With Fig. 3a, a maximum growth rate of 51 nm/min was obtained when the film was grown at room temperature and 50 W of r.f. power. Fig. 3b shows the variation of the refractive index obtained by ellipsometry measurements of the plasma polymerized organic thin films grown at different r.f. power. As the r.f. power was increased, the refractive index of thin films increased. This indicates that from the results of the electrochemical and optical properties for the ethylcyclohexane films, an organic thin film with high cross-linking, carbon contacts, and contact angle will have good corrosion protective efficiency with increasing r.f. power. The possible reason for obtaining a higher refractive index, especially at 50 W, compared with normal polymer may be due to different film thickness or surface oxidation of the as-grown films under air exposure. The other possibility is that light absorption possibly unaccounted for all data, resulting in relatively higher values than normal polymer surface.

Fig. 4 shows AFM (a–b) and cross-sectional SEM (c–d) images of the as-grown films obtained under r.f. power of 20 and 50 W, respectively. The result of AFM analysis shows that the plasma polymerized film grown at RT with 50 W r.f. power has a good r.m.s. (root-mean-square) roughness value with 1.167 nm. Also, when the plasma power was increased to 50 W, the r.m.s. roughness was decreased at room temperature. From the results of AFM, we confirmed that the surface of the polymerized film grown with 20 W of r.f. power...
is rougher than that grown with 50 W of r.f. power because of the heating effect of plasma (i.e. different surface mobility or diffusion rate). Fig. 4(c–d) show cross-sectional SEM images of the same films as Fig. 4a,b. In the cross-sectional SEM images, we recognized that a 0.5-μm-thick film with very sharp interface between the ethylcyclohexane film and silicon substrate was obtained under the condition of RF power of 50 W and Ar/H₂ = 1:1. The sharp interface suggests a good adhesion and a homogeneous film in the depth. Because if there are some oxide layers such as SiOₓ between the organic polymer and silicon substrate as well as defects as pin-holes, cracks, etc., the film adhesion and uniformity will be changed. From these SEM images, we also confirmed more smoother and featureless surfaces with increasing the r.f. power. This result can be explained by a difference of surface mobility and/or plasma density because the more high plasma power can easily break monomer and cluster in the gas phase or on the surface. In summary, the growth rate and contact angle as well as corrosion protection probability of the ethylcyclohexane thin films increase with increasing the r.f. power, while the optical transmittance and band gap decrease with r.f. power. Also, the as-grown thin films may have a high cross-linking density with increasing r.f. power.

4. Conclusions

Organic polymer thin films were deposited on glass, Si(100), and copper substrates at room temperature using an organic precursor by plasma enhanced chemical vapor deposition (PECVD) method. Ethylcyclohexane was utilized as organic precursor, and hydrogen and Ar were used as a bubbler and carrier gas, respectively. In this study, we especially compared the difference of corrosion resistant and optical properties of plasma polymerized organic thin films grown at various r.f. powers. Corrosion protection efficiency (Pₚ) examined by potentiodynamic curve measurements in 3.5 wt.% NaCl solution provided an increasing tendency with increasing RF power. The protective abilities increase with increasing r.f. power and the highest Pₚ value was 92.1% at 50 W. The as-grown organic thin films also showed quite high optical transmittance up to 85%. UV-visible results show that the as-grown films have high degree cross-linking density with increasing r.f. power. AFM and SEM data show quite smooth and dense surface morphology with increasing r.f. power. Also, the optical refractive index and contact angle are increased with increasing r.f. power. The maximum growth rate of this study is obtained to be 51 nm/min.
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References
