Wettability and Optical Properties of Organic Silicone Films via Low Temperature Plasma Deposition

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ABSTRACT

Organic materials are widely used as potielectrontic components, light emitting devices, thin film transistor(TFT) and sensor. Organic potielectronic componentsanve characteristics of thin film ans low temperature process, it is casierutilized a varied substrates than wnventional inorgnic process. The silicone films have many attracting properties such as high stability, barrier capabilities, and good transmission in the visible region of light, and can be used as a barrier coating for optical devices. In this study, plasma-deposited thin films were first prepared to obtain organic silicone containing thin films on subtrate surface. Post treatments on the SiO_x thin films by oxygen plasma treatment was then performed. Restults from WAC, AFM, SEM and WVTR show that after 15 minutes of HMDSZ (Hexamethyldisilazane) plasma polymerization, the film thickness is 84.7 nm and the water vapor transmission rate decreases to 4.66 gm/m^2-day, as compared to 6.15 gm/m^2-day of PET specimen.

Keyword：HMDSZ、water vapor transmission rate(WVTR)、UV-Vis spectrum

1. Introduction

Transparent plastics (e.g. polymetylmethacrylate, polycarbonate and polyethylene terephthalate) were increasingly demanded as their comparable light-weight in nature, sustainability under intensive impact and good process ability. However, preventing the intrusion of oxygen or carbon dioxide molecular kept these materials from practical applications. For instance in food and beverage industry, the water vapor transmission rate (WVTR) of the dump-proof package should be controlled in the range of 10–50 g/m^2 per day (specific to products with fats and oil), so as to keep the involvements fresh. In addition, electronic devices degraded frequently occurred when exposing to oxygen and moisture. Therefore, effectively excluding unexpected foreign gaseous molecules was considered potential to elongate the lifetime. As in the case of the flexible organic light emitting device (OLED), a critical value of oxygen transmission rate (i.e. less than 10^{-5} cm^3/m^2 per day) and that of WVTR (i.e. . approximately 10^{-6} g/m^2 per day should be guaranteed to ensure the reliable performance at the condition that the temperature was ~39 °C and the relative humidity was ~95%.

In light of the above, silicon oxide coatings (i.e. SiO_x) were developed onto the polymer substrates. As a result, impressive barrier effects thus the low permeability as well as the high transparency was achieved. Together with the recyclable features and their practical usage in daily life (e.g. microwave-friendly), these silicone coatings were widely accepted during recent years. In general, such coatings can be fabricated via sputtering ion beam evaporation; plasma enhanced chemical vapor deposition (PECVD). Among them, PECVD was preferred as the resultant films were flexible in addition to obtained great barrier to the foreign gaseous molecules. Moreover, silicone coatings prepared using PECVD exhibited greater adhesion to the substrate and are less prone to brittle failure than those synthesized using other physical vapor deposition methods. However, corresponding studies were of paucity thus lack of thorough understanding.

In this study, cold plasma deposition system was applied to introduce organic silicone-containing onto the glass, Si-wafer and PET substrates. Thereafter, post treatment via oxygen plasma on the HMDSZ-deposited surface was adopted. After the HMDSZ plasma treatment, the high hydrophobic (about 84°), or small contact angles were obtained on glass substrates. Observed by SEM and AFM of the film surface was smooth after HMDSZ plasma deposition time with 10 minutes, and then HMDSZ plasma deposition thickness will increase with plasma treatment time, the film thickness increase from about 26nm to 180nm.

2. Experimental procedures

2.1 Film deposition

The substrates (i.e. glass and PET) were ultrasonically cleaned with cleaning agent and distilled water at first. Further ultrasonically cleaning in ethyl alcohol was carried out followed by the air-dry at room temperature.

The plasma polymerization equipment consisted of one bell-jar reaction chamber and one 13.56 MHz radio frequency power supply (model PD-2S manufactured by SAMCO Co.) The pressure of the reaction chamber was evacuated better than 30 mTorr before deposition. HMDSZ (Hexamethyldisilazane) monomers (total amount: 100 mTorr) were then introduced into the reaction chamber. During the deposition, the substrates were left unheated. The applied power was set at 30W. To acquire different film thickness, various deposition periods (from 5 to 30 min) were adopted. Afterwards, O_2 was introduced to realize the post plasma treatment. The specific conditions included applied power of 100 W at working pressure of 40 mTorr with duration of 1 min.

2.2 Characterization

2.2.1 Chemical concentrations and morphology

The thickness of plasma polymerization films was measured using profilometer. Atomic force microscope (AFM, Digital Instrument NS3a controller with D3100 stage) operated at tapping mode was employed to obtain the surface roughness. It should be pointed out that the tip radius was less than 10 nm to enhance the resolution.

Surface morphologies of the as-deposited films were obtained using scanning electron microscope (SEM, JEOL JSM-6330F) operated at accelerating voltage of 5keV. To avoid the charging effect, all samples were coated with an Au layer in thickness of 2 nm.

The chemical compositions of the plasma deposited films were determined by X-ray photoelectron spectrometry (XPS) analysis. Spectra were recorded with a VG ESCA Scientific Theta Probe spectrometer using AlK exciting radiation. Typical operating conditions were X-ray gun, 1486.6 eV, and 6×10^{-10} Torr pressure in the test chamber.

2.2.2 Wettability

Wettability was characterized by measuring the angles (WCA) on the original substrate. A CCD camera (Microscopi Digtali Dino-Lite, AnMo Electronics Corporation) was employed to observe the topography of the distilled water droplet at room temperature. Three measurements were carried to obtain the average value. In general, smaller water contact angle indicated that the surface was more hydrophilic.

2.2.3 Optical property and water vapor transmission rate

The optical transmittance of SiOx thin films was evaluated using UV-Visible (Jasco V-560, 300 nm - 900 nm).

To date, WVTR measurement of thin films with ultra-low permeability was still a challenge. Most widely used technique of high sensitivity is the calcium degradation test, as reported in the case of OLED quality control, in which the gas permeability was limited at or less than 10^{-6} g/ m^2 per day. Mass spectrometry was another approach to measure lower value of WVTR, as reported in the test of a 1000 nm SiOx film on the PET substrate. In this study, the value of WVTR was measured using a water vapor transmission rate test system (MOCON Co., OX-TRAN® Model 2/61). The sampling size was set at 10 cm^2. Measurements were taken at atmospheric pressure and 100% relative humidity, at temperatures range of 25-40 °C. It should be noticed that all samples were kept in this condition for at least 48 h before measurement to ensure the following tests were in the equilibrium state (indicated by the constant WVTR measurements as a function of time for a given material).

3. Results and discussions

3.1 Thickness of as-deposited films and wettability

Fig. 1 shows the dependence of the HMDSZ thickness and water contact angle on the deposition time. The thickness of HMDSZ increases monotonically (from 26 to 180 nm) as deposition time increases. The calculated deposition rate is around 6.4nm/min. However, water contact angle is independent on the deposition period but retains at 84°, indicating the hydrophobic feature. The water contact angle is reduced to less than 10° as O_2 plasma treatment is applied. This decline infers that oxygen plasma treatment can largely increase the surface energy of the HMDSZ thus its hydrophilicity.

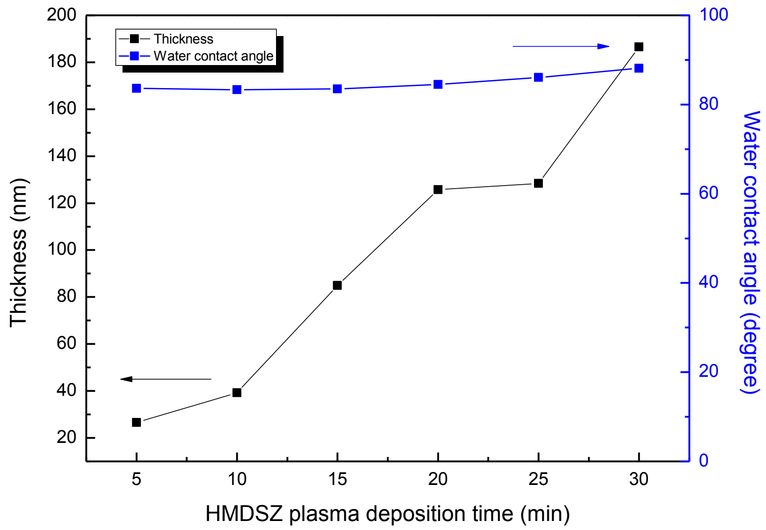

Fig.1. Variations of film thickness and water contact angles vs. time for HMDSZ plasma deposition on glass substrate.

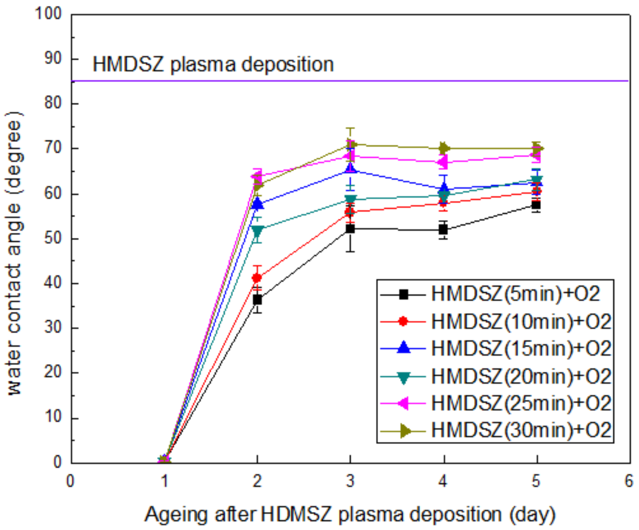

Fig.2. Variation of water contact angles of HMDSZ-deposited plus O_2 plasma treatment films on glass substrate vs. aging time.

To determine the stability of the hydrophilicity of the O_2 plasma post treated HMDSZ films, a sustainability test (at room temperature) was carried. Within five days, the evolutions of the contact angles of the as-deposited films were recorded. As seen in Fig. 2, the water contact angles of all specimens gradually increase and reach to a plateau (~70-75°). It should be noted that exposing in air leads to the hydrophilicity degradation but the water contact angle of the post treated HMDSZ is still smaller than that of pure HMDSZ.

3.2 Surface roughness and morphology

Table I summarizes the roughness of the films after plasma treatment. The arithmetic (Ra) and root mean square (Rms) roughness of bare PET are 3.38nm and 1.68 nm, respectively. After deposition of HMDSZ films, the surface becomes smoother. However, the surface becomes even smoother after oxygen plasma treatment.

Table.I. The arithmetic (Ra) and Root-mean-square (Rms) roughness of the O_2 post treated HMDSZ surface

HMDSZ plasma deposition time (min)	HMDSZ plasma deposition		Oxygen plasma treatment	
	Rms (nm)	Ra (nm)	Rms (nm)	Ra (nm)
PET substrate	3.38	1.68	-	-
10	1.46	0.88	1.28	0.86
15	1.40	0.78	0.57	0.49
20	3.26	1.62	1.37	0.80
25	1.37	0.89	1.19	0.83
30	1.51	1.04	0.54	0.42

Fig. 3(a) illustrates the untreated PET substrate. The surface is extremely smooth, in correspondence with the results from AFM. Fig. 3(b) demonstrates the PET substrate coated with conformable and dense HMDSZ films. Good coverage reduces the chances of the occurrence of pinhole originated form filler particles and debris (i.e dust) presented on the surface. However, more stack structures are observed in the O_2 plasma treated HMDSZ coatings, as shown in Fig. 3(c).

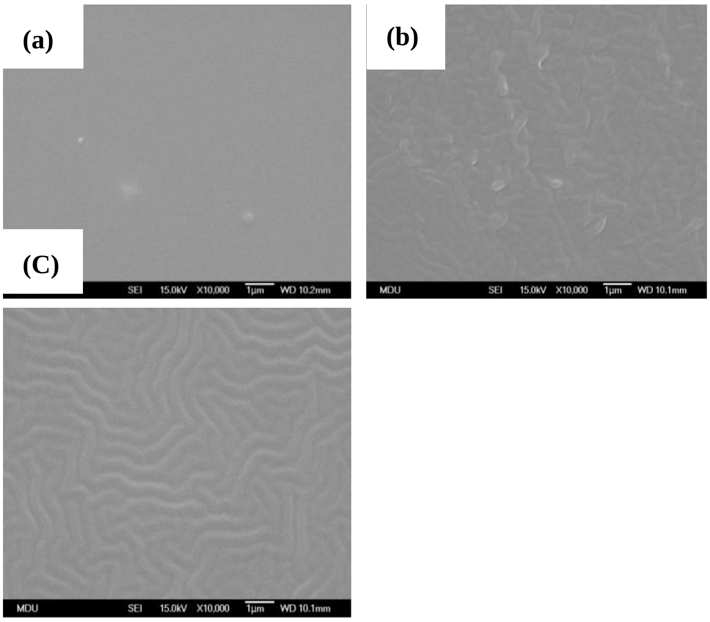

Fig. 3. SEM images of the surface of (a) uncoated PET, (b) HMDSZ (~120 nm) coated PET and (c) O_2 plasma treated HMDSZ

3.3 Chemical structure of Plasma Polymer Films

Table 2 lists the chemical compositions of HMDSZ film with or without O2 plasma treatment on the PET surface. The chemical concentrations are calculated from the C 1s, O 1s, N 1s and Si 2p peaks. The concentration of C and N decreases after oxygen plasma treatment, while that of Si retains the same. The chemical concentration of O increases by a large extent. Consequently, the O/Si ratio increase greatly from 0.38 to 1.47 after post treatment.

Table 2. Chemical compositions of HMDSZ films

	Composition (at.%)				Atomic ratio
Elements	C	O	N	Si	O/Si
1	50.32	10.77	11.09	27.81	0.38
2	25.86	42.27	3.12	28.75	1.47

1. HMDSZ 2. O_2 treated HMDSZ

3.4 Optical properties and water vapor transmission rate

Fig.4 illustrates the transmittance spectra of the HMDSZ films on glass substrate. In visible light region, a high transmittance ~90% is reached. The transmittance spikes up to ~98% after oxygen plasma treatment, indicating the great potential for optical applications.

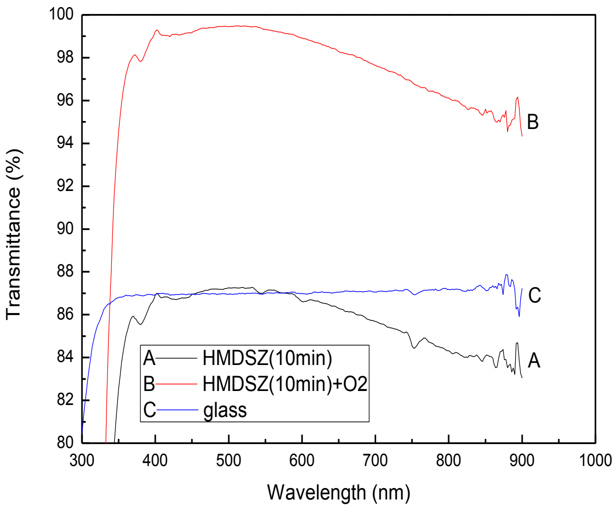

Fig. 4. The transmittance spectra of HMDSZ films deposited on glass substrate.

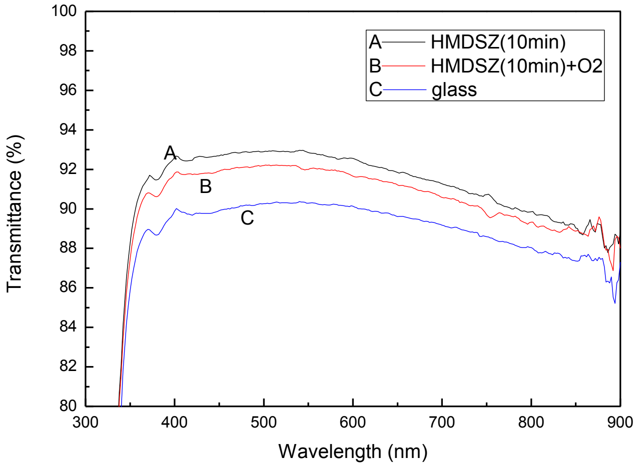

Fig. 5 shows the transmittance spectra of HMDSZ films on glass substrate after five days exposing in air. However, oxygen plasma treatment is close to the original glass about 88%.

Fig. 6 displays the WVTR curves of pure PET, PET with HMDSZ films, PET with HMDSZ films treated by O_2 plasma. Among them, PET with HMDSZ (84.94 nm in thickness) performs best as the lowest WVTR of 4.66gm/m2 per day. However, PET with HMDSZ film treated by O_2 plasma exhibits the same WVTR as pure PET, inferring that O2 plasma induce no positive effect on the WVTR.

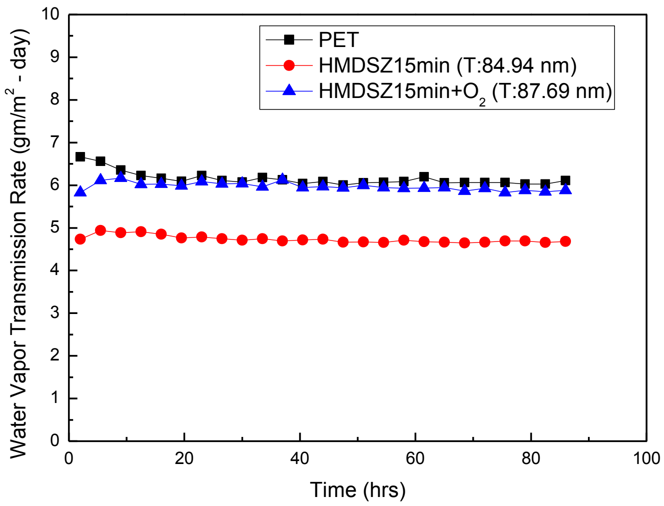

Fig.6. The water vapor transmission rate of HMDSZ-deposited films on PET substrate

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4. Conclusion

In this study, a specific silicone film is developed via PECVD technique. The major conclusions are itemized as follows:

1. HMDSZ plasma treatment lead to the hydrophobic feature on the surface (water contact angle at 84°), while post O_2 plasma treatment results in drastic increase of surface energy thus the small contact angles.
2. The synthesis of HMDSZ using PECVD is efficient as its high deposition rate (6.4 nm/min).
3. HMDSZ films with O_2 plasma treatment can enhance the transmittance as compared to the glass and pure HMDSZ films.
4. PET with HMDSZ film performs better than the pure PET and PET with HMDSZ treated by O_2 plasma in the test against water vapor. The water vapor transmission rate of only 4.66 gm/m^2 per day guarantees its potential in packaging food and beverage.

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