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Gas permeation properties of silicon oxynitride thin films deposited on polyether sulfone by radio frequency magnetron reactive sputtering in various N_2 contents in atmosphere

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ABSTRACT

A silicon oxynitride (SiO_xN_y) thin film was deposited on polyether sulfone (PES) as a barrier layer against water vapor permeation using reactive radio frequency (RF) magnetron sputtering with a pure Si target in an Ar/N_2 atmosphere. The coating parameters studied included RF power, N_2 content in atmosphere and substrate bias. The water vapor transmission rate, thickness, chemical bonds, microstructure and light transmittance of the films were measured. Taguchi analysis shows that the N_2 content has the most significant influence on the permeability of the gas barrier films. Experimental results show that using a fixed working chamber pressure of 1.6 Pa and deposition time of 30 min results in the lowest water vapor transmission rate which is two orders of magnitude smaller than that of uncoated PES; this result was obtained with an RF power of 250 W, N_2 content of 100% and without applying substrate bias. By precisely adjusting the N_2/Ar flow ratio, the largest light transmittance was obtained, at 95% N_2. It was also found that the gas barrier properties of the SiO_xN_y film are heavily influenced by its microstructure.

1. Introduction

Flexible flat panel displays (FPDs) are one of the most attractive state-of-the-art products and have the potential to revolutionize our daily lives. One of the main challenges for the development of a durable flexible FPD is the degradation of electronic materials within the FPD due to moisture or oxygen permeation. This problem is especially severe when one uses a polymer substrate, which normally possesses insufficient resistance against gas permeation [1]. Polymers used in such devices should be flexible, light-weight, transparent, highly elastic, with easy handling and low material and process costs.

In the past decade, many attempts to enhance gas permeation resistance of polymer substrates have been made. Among them, the use of a barrier layer seems to be one of the most promising methods [2–6] and much attention has been paid to polyethylene terephthalate (PET), due to its popularity. However, PET's low glass transition temperature of 342 K [7] limits its use, both in process and application. On the other hand, polyether sulfone (PES), with a glass transition temperature of 498 K and a stable thermal expansion coefficient of 5.5×10^{-5}/K [8] ($<2 \times 10^{-5}$/K for glass fiber enhanced), is a promising potential candidate for flexible FPD. PES is non-crystalline and light amber in color; there are only a few reports about the reduction of gas permeability of PES using barrier layers [9,10]. Most recently, J. Shim et al. [11] prepared a silicon oxynitride (SiO_xN_y) gas barrier coating on PES using plasma-enhanced chemical vapor deposition. A Si-based undercoat layer was used as an interfacial buffer between PES and SiO_xN_y and the optimal oxygen transmission rate was 0.2 cm^3/m^2 day measured at 35 °C and 0% relative humidity.

Amorphous SiO_xN_y thin films [12] have excellent thermal and chemical stability and are widely used as a passivation layer in the semiconductor industry. In this study, a reactive radio frequency (RF) magnetron sputtering system was used to deposit SiO_xN_y films onto clean PES surfaces. A pure Si target and pure nitrogen gas are used as the reacting elements. Three sputtering parameters – RF power, N_2 flow ratio and substrate bias – were varied and the results were analyzed using the Taguchi method; the two dominating parameters were fine-tuned in order to investigate their influence on gas permeation through SiO_xN_y films.

2. Experiments

The sputtering system used in this study was made by BRANCHY Technology Corp. Its vacuum system is a turbo molecular pump system with a base pressure of 2.6×10^{-3} Pa. The RF generator and matching box were Cesar 136 and WM1000A/AW from DRESSLER Corp., respectively. A 4 in. diameter, 6 mm thick 5 N Si target was used and the target-to-substrate distance was 9 cm. 5 N nitrogen gas was used as the reactive agent and was mixed with 5 N Ar in varying ratios. No oxygen flow was introduced. 200 μm thick PES foil was purchased from

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Table 1
Experimental conditions for sputtering deposition.

Parameters	1st stage	2nd stage
N_2 content in atmosphere (%)	50, 75, 100	50–100 in a step of 5
RF power (W)	200, 250, 300	250
Substrate bias (V)	0, −30, −60	0

ZENCATEC Corp. and was cut into 4.5 × 4.5 cm^2 and 2 × 2 cm^2 pieces, cleaned with anhydrous alcohol and dried in draught.

PES substrates were pre-sputtered using a −300 V bias in Ar plasma at 1.6 Pa for 10 min to remove contaminants and activate the surface. The SiO_xN_y films were prepared under 27 conditions, which were combinations of varied N_2 contents in atmosphere (50%, 75% and 100%), RF power (200, 250 and 300 W), and substrate bias (0, −30 and −60 V). The total flow rate was 25 sccm and the deposition time was fixed at 30 min. The temperature of the substrate surface was neither monitored nor controlled during sputtering. However, from minor flection of PES foil substrate after sputtering, the temperature of the substrate should not exceed 200 °C. The water vapor transmission rate (WVTR) of the films was measured using a MOCON Permatran-W Model 3/61. The test temperature and relative humidity were 40 °C and 100%, and the flow rate of nitrogen and water vapor was 10 and 30 sccm, respectively. The lower limit of detection is 0.05 g/m^2 day. The data obtained during this first stage were analyzed using the Taguchi method in which a lower WVTR was interpreted as advantageous. The most dominating parameter was chosen accordingly and varied for the second stage of sputtering deposition. The experimental conditions for the first and second stages are listed in Table 1.

In addition to WVTR, the thickness and roughness, microstructure, IR absorbance, and optical transparency of the SiO_xN_y films prepared after the second stage were measured using a VEECO Dektak ST surface profiler with a resolution of 0.1 nm, a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM), a PERKIN ELMER RX-I Fourier-transform infra-red spectrometer (FTIR) and a HITACHI U3010 UV–visible adsorption spectrometer. The operating voltage of FE-SEM was 3 kV. For quantitative determination of bonding states from corresponding peaks in a IR spectrum, a baseline for each peak was drawn and the height of the peak was measured. The effects of RF power and N_2 flow ratio on the film properties are reported and discussed below.

Table 2
Orthogonal arrays of the experimental data of the SiO_xN_y films deposited on PES at the first stage.

No.	RF power (W)	N_2 content (%)	Substrate bias (V)	WVTR ($g/m^2 \cdot day$)	S/N
1	200	50	0	29.0	−29.4
2	200	50	−30	28.0	−28.9
3	200	50	−60	25.0	−27.9
4	200	75	0	33.0	−30.3
5	200	75	−30	6.7	−16.5
6	200	75	−60	29.0	−29.2
7	200	100	0	30.0	−29.5
8	200	100	−30	2.6	−8.2
9	200	100	−60	34.0	−30.6
10	250	50	0	4.8	−13.6
11	250	50	−30	18.5	−25.3
12	250	50	−60	51.1	−34.1
13	250	75	0	34.2	−30.6
14	250	75	−30	33.0	−30.3
15	250	75	−60	5.9	−15.4
16	250	100	0	0.5	−7.9
17	250	100	−30	28.0	−28.9
18	250	100	−60	4.1	−12.2
19	300	50	0	11.1	−20.9
20	300	50	−30	17.0	−24.6
21	300	50	−60	9.5	−19.5
22	300	75	0	18.5	−25.3
23	300	75	−30	28.0	−28.9
24	300	75	−60	9.2	−19.2
25	300	100	0	23.0	−27.2
26	300	100	−30	11.5	−21.2
27	300	100	−60	2.4	−7.6

Table 3
Responsive results from Table 2.

RF power (W)	$\sum S/N/n$ WVTR	N_2 content (%)	$\sum S/N/n$ WVTR	Substrate bias (V)	$\sum S/N/n$ WVTR
200	−25.61	50	−25.04	0	−25.81
250	−22.08	75	−25.12	−30	−23.68
300	−21.62	100	−19.29	−60	−21.98
$\sum S/N/n_{max} - \sum S/N/n_{min}$		$\sum S/N/n_{max} - \sum S/N/n_{min}$		$\sum S/N/n_{max} - \sum S/N/n_{min}$	
3.99		5.72		3.83	

3. Results and discussion

Table 2 presents the orthogonal arrays of the experimental data of the SiO_xN_y films deposited on PES after the first deposition stage. The signal-noise-ratio (S/N) value was calculated as:

$$S/N = -10 \times \log\left(\frac{1}{n}\sum_{i=1}^{n} y_i^2\right) \tag{1}$$

where y_i is the individual experimental result (WVTR, in this case), and n is the number of results.

The corresponding responsive results are shown in Table 3. It is found that the order of the influence factor of the three sputtering parameters on WVTR of the SiO_xN_y film is:

N_2 content (5.72)>RF power (3.99)>substrate bias (3.83).

Note that the difference between the last two is not very significant.

The lowest WVTR was found for the SiO_xN_y film deposited at an RF power of 250 W, N_2 content of 100% and substrate bias of 0 V. At the beginning of the second stage of experiments, the N_2 content in atmosphere was the single process variable, ranging from 50% to 100% N_2 content, and the other two parameters were fixed (cf. Table 1). The WVTR of PES coated with SiO_xN_y films deposited using various N_2 contents in atmosphere are plotted in Fig. 1. In general, the resistance against water vapor permeation of all PES samples exceeds that of uncoated PES (52 $g/m^2 \cdot day$). The WVTR decreases as N_2 content increases from 50% N_2 and reaches a local minimum of 1 $g/m^2 \cdot day$ at 60% N_2. This increases to a maximum of 34 $g/m^2 \cdot day$ with 75% N_2. For higher percentages the WVTR plateaus at around 25 $g/m^2 \cdot day$ and, as the inlet gas is pure N_2, the SiO_xN_y coated PES sample possesses the best

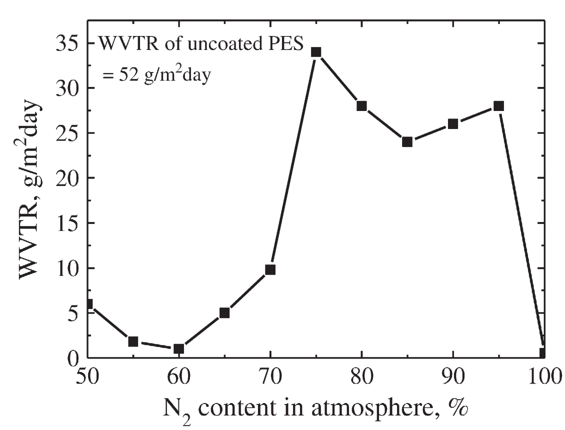

Fig. 1. WVTR of PES coated with the SiO_xN_y films deposited at various N_2 contents in atmosphere.