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Influence of film structure on gas barrier properties of SiO_xN_y films

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ABSTRACT

SiO_xN_y thin films were deposited on PET substrates by dc magnetron sputtering under various nitrogen gas flow ratios, and the influence of the nitrogen gas flow ratio on the gas barrier performance was examined on the basis of local structure of SiO_xN_y. The surface morphology of the films was evaluated by FE-SEM and AFM observations. The local structure of SiO_xN_y was determined by FT-IR analysis and measurement of refractive index. No obvious macro-defects, such as pinholes, were observed in the films and the surface morphology of all samples was similar. The film density increased with increasing nitrogen gas flow ratio during the deposition process. However, the gas barrier performance decreased with increasing nitrogen gas flow ratio. On the basis of FT-IR analysis, it was determined that the structure of the SiO_xN_y film was a random bonding model (RBM) structure and an increase in the nitrogen gas flow ratio caused an increase in hydrogen termination in the Si–O–N network. The degradation of gas barrier performance at a high nitrogen gas flow ratio is due to the discontinuous Si–O–N network caused by the hydrogen termination.

1. Introduction

Coating a thin film is one method to prevent the penetration of oxygen and water vapor into a polymer. A traditional and popular film material is aluminum which is deposited onto the polymer by vacuum deposition. Aluminum films yield good gas barrier performance [1–3] and are widely used for food packaging. However, the opaque aluminum film is limited in use because transparent packaging materials are required to confirm the state of the content after production.

AlO_x and SiO_x films are popular transparent materials that are used with polymer substrates as gas barrier films. The films are deposited by various methods and their gas barrier performance has been studied by many researchers [3–10]. Recent applications demand higher gas barrier performance from the packaging, for instance for longer shelf life; however, it is difficult to realize the required higher performance by using oxide films. For better gas barrier performance, two film materials, DLC [11–15] and silicon oxynitride (SiO_xN_y) [16–18], appear to be promising. In particular, SiO_xN_y films clearly show higher gas barrier performance compared to SiO_x films [18].

The gas barrier performance depends on various factors, including defect size [19–21], film thickness [20], film density [22] and substrate roughness [23]. In particular, defect size is important to obtain higher gas barrier performance. Rossi et al. reported that gas barrier performance is more sensitive to many small holes in a barrier layer rather than few large holes when the total area of holes is the same [19]. In addition, Roberts et al. proposed that the gas permeation process in barrier films consists of three components: unhindered transport through 'macro-defects' (>1 nm), hindered transport through 'nano-defects' (<1 nm), and hindered transport through the amorphous lattice of the oxide (interstice <0.3 nm), and they suggested that nano-defects increase the magnitude of the permeability for relatively large molecules such as oxygen at room temperature for SiO_x films wherein no obvious macro-defects were observed [20]. Grüniger also reported, based on numerical calculations, that small and compact defects are most effective in destroying barrier performance [21]. Thus, evaluation of small defects is important for gas barrier films.

In this study, SiO_xN_y films were deposited onto PET substrates by a dc magnetron sputtering method under various inlet nitrogen flow ratios. The influence of nitrogen gas flow ratio on the oxygen gas barrier performance is discussed on the basis of defects and local structure in the film.

2. Experimental

SiO_xN_y films were coated by a dc magnetron sputtering method onto 150×50 mm PET substrates (32-μm thick, general purpose grade, Okura Industrial Co., Ltd., Japan). The substrates were cleaned carefully using an ultrasonic bath in acetone prior to deposition. The cleaned substrates were placed on a holder in a vacuum chamber. After the chamber was evacuated to 4.0×10^{-3} Pa, process gases were introduced into the chamber through mass flow controllers. To deposit SiO_xN_y films, a gas mixture of argon (>99.999%) and nitrogen

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gas (>99.995%) was used as the process gas without oxygen. This is because SiO_xN_y films are obtained when oxygen gas as a process gas is introduced into the chamber with other process gases. Therefore, residual oxygen and oxygen desorption from the chamber walls was used as the oxygen source for the SiO_xN_y films [18] in this work. A pre-sputtering treatment was carried out in argon atmosphere for 1 min to remove surface contamination and any oxidation layer of the target. The SiO_xN_y film was then deposited onto one side of the PET substrate using a boron-doped silicon plate target. Details of the conditions used are shown in Table 1. The processing time was adjusted to produce a film about 30-nm thick.

The oxygen transmission rate (OTR) was measured using OX-TRAN (OX-Tran 2/20, Mocon, USA) at 23 °C and 0% relative humidity. The film thickness was determined by measuring the peak-valley height between the uncoated and coated areas using a stylus surface profilometer (Dektak3, Veeco Instruments, USA). The surface morphology of the film was observed using a field emission scanning electron microscope (S4700, HITACHI, Japan) and atomic force microscope (AFM: SPA300, Seiko Instruments, Japan). Measurement of film thickness and surface observations were performed using a stainless steel substrate because it was difficult for the PET substrate to be fixed accurately and flat on a stage for high magnification observations. However, we compared the OTR of the SiO_xN_y/PET sample and the oxidation behavior of the SiO_xN_y/stainless steel sample in our previous work and confirmed that they showed good agreement [24]. A Fourier-transform infrared spectroscope (Nicolet 380, Thermo ELECTRON Corp., Japan) was used to analyze the chemical bonds of the SiO_xN_y films. The films were analyzed at room temperature in air by the attenuated total reflection (ATR) method using a Ge prism. A UV–visible light spectroscope (V-570, JASCO Corp., Japan) was used to evaluate the optical transparency and the refractive index of the films.

3. Experimental results

3.1. Oxygen transmission rate and optical transparency

In order to examine the effect of the nitrogen gas flow ratio on the gas barrier properties of the SiO_xN_y films, OTR was measured using just a PET sheet as well as PET sheets with SiO_xN_y thin films deposited at various nitrogen gas flow ratios, $N_2/(Ar+N_2)$. Two samples were prepared for each nitrogen gas flow ratio.

The results are shown in Fig. 1 as a function of the nitrogen gas flow ratio. The OTR of the PET substrate without any film was about 35 cc/m^2 day atm. For the coated samples, the OTR of all the samples clearly improved. However the OTR of the coated samples depended on the nitrogen gas flow ratio during deposition. It was almost constant below a $N_2/(N_2+Ar)$ value of 0.12, less than 2.0 cc/m^2 day atm. In this range, the minimum OTR was 0.71 cc/m^2 day atm obtained at a $N_2/(N_2+Ar)$ value of 0.04. This value is equivalent to or better than those reported for films which show good barrier properties such as PET/SiO_x [6], PET/DLC [13,14] and PET/AlO_x [4]. However, the OTR rapidly increased with increasing nitrogen gas ratio above $N_2/(N_2+Ar)$ of 0.12. The OTR at $N_2/(N_2+Ar)$ of 0.16 was about 5.0 cc/m^2 day atm.

Table 1
Sputtering conditions.

Target	Si
Substrate	PET
Ar gas flow rate, sccm	53.8–61.4
N_2 gas flow rate, sccm	2.6–10.2
N_2 gas flow ratio: $N_2/(N_2+Ar)$	0.04–0.16
Target current, A	0.5
Bias voltage, V	−60
Coil current, A	20
Anode voltage, V	4
Base pressure, Pa	2.50×10^{-3}
Deposition pressure, Pa	0.57
Heater temperature, K	R.T.
Film thickness, nm	30

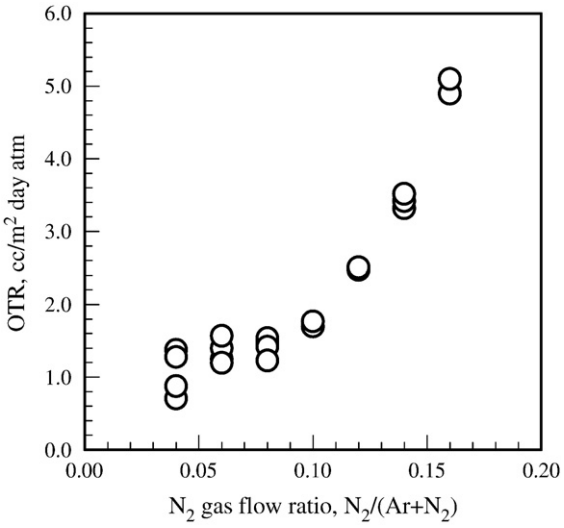

Fig. 1. Oxygen transmission rates as a function of nitrogen gas flow ratio $N_2/(N_2+Ar)$ during deposition (OTR PET: 35 cc/m^2 day atm).

Fig. 2 shows the optical transparency of PET/SiO_xN_y films. The transparency above $N_2/(N_2+Ar)$ of 0.10 was equivalent to that of uncoated PET. In contrast, the transparency decreased with decreasing nitrogen gas flow ratio below $N_2/(N_2+Ar)$ of 0.10. In the case of deposition under low nitrogen gas flow ratios, the oxygen content in the film will be insufficient to obtain high transparency.

3.2. Surface morphology

SEM and AFM observations were carried out to examine the effects of the nitrogen gas flow ratio on the formation of macro-defects in the film such as cracks, pinholes and grain boundaries. Fig. 3 shows typical film surfaces observed by FE-SEM for $N_2/(N_2+Ar)=0.06$ which showed high barrier properties, $N_2/(N_2+Ar)=0.10$ at which degradation of the gas barrier properties began, and $N_2/(N_2+Ar)=0.14$ which showed low barrier properties. All substrates were completely covered by the films and there were no obvious cracks

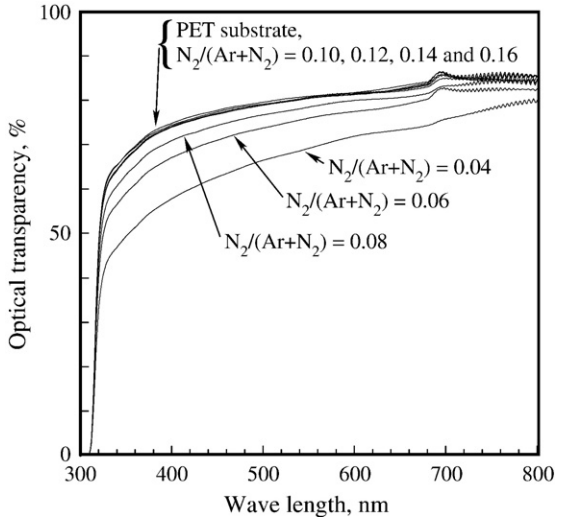

Fig. 2. Optical transmittance of SiO_xN_y films deposited under various nitrogen gas flow ratios.