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Estimation of moisture barrier ability of thin SiNx single layer on polymer substrates prepared by Cat-CVD method

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Abstract

The SiNx films with the thickness of 50 nm were prepared by Cat-CVD method on the cyclic olefin copolymer (COC) and the polyethylene terephthalate (PET) substrates, and their moisture barrier abilities were evaluated. MOCON measurement method and Ca degradation test showed the moisture permeation results of 0.02 g/(m^2 day) for PET substrate and 0.006 g/(m^2 day) for COC substrate after SiNx deposition. Applying the simple model of gas barrier property, it was estimated that the Cat-CVD method achieves the high coverage ratio of over 99% for SiNx film on these substrates, and the moisture permeation rate of single SiNx film with the thickness of 50 nm was estimated to be 0.0045 g/(m^2 day).

Keywords: Gas barrier film; Cat-CVD

1. Introduction

For the application of mobile displays or large-scale displays such as liquid crystal display (LCD), organic light emitting diode (OLED) display, e-paper driven by electrophoresis, etc., transparent polymer films are favourable substrates due to their lightweight and flexible properties. However, the polymer itself has poor gas barrier ability for moisture and oxygen, which can cause the degradation of switching materials, light emitting materials, and so on. Therefore, it is necessary to coat the transparent layers with the moisture and oxygen barrier layers on the polymer films in order to improve the reliability of these devices.

The SiNx film prepared by catalytic chemical vapor deposition (Cat-CVD) method, which has transparency and high gas barrier ability even at a low deposition temperature, has been proposed for this solution [1].

In this study, we investigated the moisture permeation rate of thin Cat-CVD SiNx single layer prepared on polymer substrates, and estimated the coverage ratio on these polymer substrates and intrinsic moisture barrier ability about this SiNx film with a thickness of 50 nm.

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2. Experimental details

Cyclic olefin copolymer (COC) film with a thickness of 100 μm and the surface smoothened polyethylene terephthalate (PET) film with a thickness of 125 μm were used as substrates. SiNx films with the thickness of 50 nm were prepared by Cat-CVD method using SiH_4, NH_3 and H_2 gas mixture compositions, which were decomposed on a tungsten catalyser heated around 1800 °C. The substrate holder was located at the bottom of chamber, and the distance between the catalyser and the substrate was 200 mm. The 10 cm^2 size substrate was held on the holder by sticking polyimide tape at the corner of substrate. The substrate temperature was kept below 100 °C during the deposition by cooled substrate holder.

Surface roughnesses and morphologies of bare substrates and deposited SiNx surfaces were measured by atomic force microscopy (AFM).

Moisture permeation rates were examined with the MOCON measurement system under the conditions of 40 °C and 100% relative humidity, whose detection limit was around 0.005 g/(m^2 day). The samples, whose moisture permeation rates were around the detection limit of MOCON measurement, were examined by Ca degradation test under the conditions of 40 °C and 90% relative humidity to evaluate the exact moisture permeation rates.

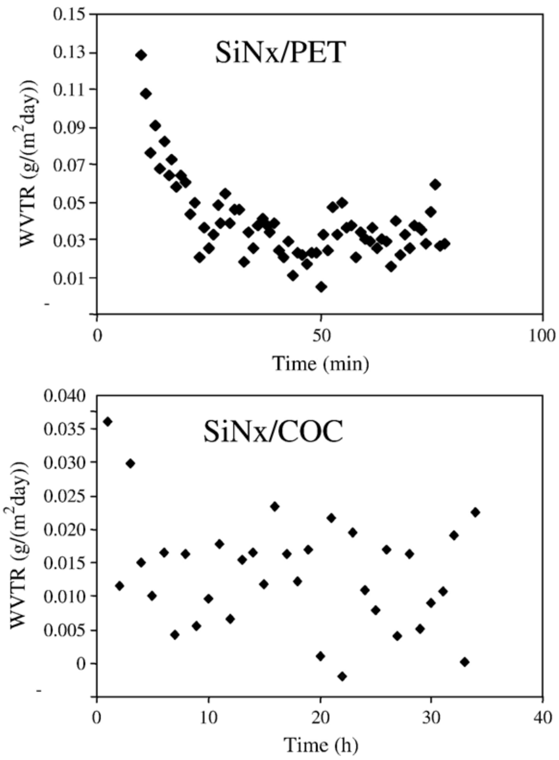

Fig. 1. Water vapor transmission rate (WVTR) i.e. moisture permeation rate of SiNx/PET and SiNx/COC by MOCON measurement.

In this measurement, the samples were prepared as follows; 1) the samples were degassed in the vacuum oven around 90 °C for 6 hours, 2) metal electrodes and Ca film were deposited on the SiNx layer, 3) Ca film was encapsulated by the epoxy sealant and glass plate with getters. The moisture permeation rate was calibrated from the conductivity change of the Ca film, that is caused by the reaction between Ca and permeated H_2O through the COC substrate and SiNx layer in temperature and humidity controlled chamber [2].

Furthermore, for the samples kept in the humidity chamber under the conditions of 40 °C and 90% relative humidity, increase of Ca film degradation on SiNx layer was monitored through the glass plate with an optical microscope to investigate the defect signatures in SiNx film. The colour contrast between oxidized and non-oxidized Ca was used in this qualitative analysis. The images were taken at intervals of typically several hours. From the images the Ca-corroded spots could be directly linked to defects of the barrier films [3].

3. Results

The SiNx deposited substrates didn't have notable curving, probably due to the low stress of SiNx film by Cat-CVD method [4].

Moisture permeation rates under the condition of 40 °C and the 100% relative humidity of bare COC film and surface smoothened PET were measured by the MOCON method. They were found to be 0.53 g/(m^2 day) and 5.3 g/(m^2 day), respectively.

Fig. 1 shows the MOCON measurement results of 50-nm-thick SiNx-deposited surface-smoothened PET film and COC film. Steady state permeation rate of SiNx/PET is about 0.02 g/(m^2 day). However, the result of SiNx/COC shows the scattering around the detection limit. Therefore, the moisture permeation rate of SiNx/COC was examined by measuring conductivity change of Ca film, and two different slopes were observed as shown in Fig. 2. It can be considered that the first slope shows the initial non-steady state water vapor de-sorption from the COC film. However, the second slope shows the steady state moisture permeation rate of SiNx/COC sample, where the rate of absorption, the diffusion rate across the barrier and the rate of de-sorption are constant. The moisture permeation rate was estimated to be 0.006 g/(m^2 day) from steady state region. We confirmed the reproducibility of these results with multiple samples, and the best results were around 0.006 g/(m^2 day) for SiNx/COC and around 0.02 g/(m^2 day) for SiNx/PET.

4. Discussion

According to the Oxford defects model [5], which analyses theoretically the gas permeation properties of inorganic gas barrier layer(s) deposited on polymer film, the defects in inorganic gas barrier layer(s) are categorized into three ranks by their sizes. The smallest one is 'lattice defects' with the size below 3 Å, where the gas species diffuse through amorphous lattice, and the largest one is the 'macro defects' with the size over 10 Å, where the gas species can pass through it directly. Middle size of these is defined as 'nano defects' with the size between 3 Å and 10 Å, where the gas species diffuse through the relatively narrow passages. Fig. 3 shows the degradation growth of Ca film on a part of SiNx/COC from initial state to 76 hours exposure in the humidity chamber. Three defects are observed from 24 hours, and these defects grow larger as the exposed time increases. However, the number of defects does not increase and remains at three even after 76 hours of exposure.

Therefore, it can be considered that the SiNx film itself is stable for the exposure to humidity, and the moisture permeation properties of these samples are dominated by pinholes i.e. 'macro defects', which may be introduced at the initial stage of SiNx deposition due to the film surface morphology and defects.

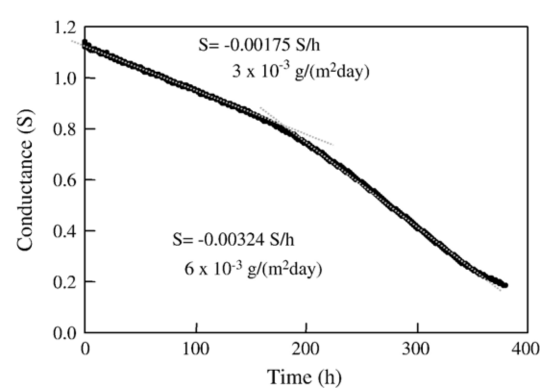

Fig. 2. Conductivity change of Ca film on SiNx/COC.