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Reduced water vapor transmission rates of low-temperature-processed and sol-gel-derived titanium oxide thin films on flexible substrates

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ABSTRACT

Sol-gel-derived, crack-free, and condensed TiO_x thin films with improved barrier properties were successfully fabricated on polymeric substrates with a simple two-step heat treatment at low temperatures. To assess the barrier properties of the TiO_x thin films, Ca corrosion tests were conducted and their water vapor transmission rates (WVTRs) were measured. We found that the two-step heat treatment (at 45 °C for 90 min and 110 °C for 60 min) produces a close-packed TiO_x structure that substantially reduces the WVTRs of the coated polymeric substrates. The WVTRs of 86 nm thick TiOx thin films on polyethylene naphthalate (PEN) substrates at a relative humidity (RH) of 90% were found to be 0.133 g m^{-2} day^{-1} at 38 °C and 0.0387 g m^{-2} day^{-1} at 25 °C. In addition, the WVTR value of the TiO_x thin films on PEN substrates are stable with respect to bending: it was found to increase by only ~13% after 100 repetitions of bending with a 20 mm radius.

1. Introduction

The fabrication of thin-film passivation layers that prevent the penetration of oxygen and water vapor remains a major challenge in the fields of food packaging, medicines, and electronics [1–4]. Reactive gases (e.g., O_2) and water molecules can cause electrical instability in thin-film electronic devices [5–8] and reduce the lifespans of low work function metal electrodes [9]. In fact, the fabrication of suitable barrier films with solution-based, low-cost, and low-temperature routes is the primary hurdle to the development of organic and/or flexible electronic and optoelectronic devices. The required water vapor transmittance rates (WVTRs) are known to be typically in the range of 10^{-1} g m^{-2} day^{-1} ~ 10^{-3} g m^{-2} day^{-1} for organic transistors, ~10^{-4} g m^{-2} day^{-1} for organic photovoltaics, and ~10^{-6} g m^{-2} day^{-1} for organic light-emitting diodes [1,2,4]. Barrier films that meet these standards and that can be prepared with simple and low-temperature solution processes are required.

Of the various candidates for such barrier films, inorganic thin films such as vacuum-deposited titanium oxide (TiO_x) and aluminum oxide (AlO_x) [10–12] exhibit excellent intrinsic gas barrier properties. However, they have a number of disadvantages when used in organic electronic devices: 1) they are prone to cracking when flexed [4], 2) they are not suitable for large-area applications because of their expensive and complicated processing environments (e.g. a vacuum and/or an inert environment), and 3) it is difficult to prepare organic-inorganic multi-layered barrier films on polymeric materials [13–15].

In contrast, sol-gel-derived inorganic thin films have received much attention as promising candidates for barrier films because of their simple, cost-effective, and large-area processability. In particular, sol-gel-derived TiO_x thin films have been extensively tested as encapsulation layers for organic thin-film electronic and

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optoelectronic devices such as organic field-effect transistors, polymer light-emitting diodes, and organic photovoltaic cells [16,17]. Previous reports have demonstrated that TiO_x thin films exhibit good barrier properties against oxygen and moisture in ambient air and that devices with TiO_x encapsulation layers exhibit improved lifetimes. However, these studies primarily focused on the time-dependent performances of devices with and without encapsulation layers rather than on the intrinsic properties of the TiO_x films such as their gas barrier properties and thin-film flexibilities. In fact, the WVTRs of sol-gel-derived TiO_x thin films have not yet been systematically studied and the feasibility of using sol-gel-derived TiO_x thin films in flexible thin-film applications has never been demonstrated. In order to utilize sol-gel-derived TiO_x thin films in organic electronic devices, they require improved WVTRs, and thus we need to improve our understanding of their barrier properties. In addition, it is also vital to investigate their mechanical properties and in particular their bending stabilities because such encapsulation layers are part of flexible organic electronic devices.

Further, decreasing the processing temperature of sol-gel-derived TiO_x thin films is another research priority because such films typically require a high-temperature annealing step if they are to have a densely packed structure. However, annealing at high temperatures (>200 °C) is not compatible with conventional polymeric substrates. Thus, to use sol-gel-derived TiO_x thin films as barrier films in organic electronic devices, it is important to fabricate crack-free and condensed TiO_x thin films at low temperatures and to improve our understanding of their barrier properties as well as of their mechanical bending stabilities.

In this study, we investigated the water-vapor barrier properties of TiO_x thin films prepared with a sol-gel method consisting of a simple two-step heat treatment at low temperatures on polymeric substrates, particularly polyethylene naphthalate (PEN). Crack-free TiO_x thin films were obtained on PEN substrates by controlling the film thickness, and the effects of the two-step heat treatment were investigated by analyzing the thicknesses, morphologies, refractive indices, and FTIR spectra of the TiO_x thin films. We found that evaporating solvents at 45 °C for 90 min prior to the thermal annealing of the TiO_x thin films resulted in more efficient polycondensation during the sol-gel reaction, thereby enabling the fabrication of TiO_x thin films with close-packed structures at low temperatures around ~110 °C. Ca corrosion tests were performed under various atmospheric conditions to measure the WVTRs of the TiO_x thin films. The WVTR of 86 nm thick TiO_x thin films on PEN substrates was found with the Ca corrosion test measurements to be 0.133 g m^{-2} day^{-1} at 38 °C and 90% relative humidity (RH). The WVTR value at 25 °C and 90% RH was calculated by extrapolation from the values of WVTRs at other temperatures and found to be 0.0387 g m^{-2} day^{-1}. In addition, we examined the effects of mechanical bending stress on the WVTRs of the TiO_x thin films on PEN substrates and found that the WVTR increases only by ~13% from its initial value after 100 bending repetitions with a bending radius of 20 mm.

2. Experimental section

TiO_x-based solutions were prepared by using titanium isopropoxide (purchased from Aldrich) as the precursor, absolute ethanol (purchased from Aldrich) as the solvent, and hydrochloric acid (purchased from Aldrich) in de-ionized water as the catalyst to promote hydrolysis. The titanium isopropoxide concentration was 0.4 mol/L, the water to titanium isopropoxide molar ratio was 0.82, and the theoretical solution pH, calculated from the amount of hydrochloric acid, was 1.27.

The TiO_x solutions were spin-coated at 1000 rpm for 60 s onto silicon wafers and the polymeric substrates PEN (purchased from SKC) and polyimide (PI, purchased from SKC Kolon PI). The TiO_x solutions were diluted with absolute ethanol and the spin rate was modulated from 1000 rpm to 4000 rpm to control the film thickness. The TiO_x thin films were pre-heated at 45 °C for 90 min and post-heated at temperatures ranging from 110 °C to 500 °C on a hot plate for 1 h. All experiments were performed in ambient air.

The thicknesses and refractive indices of the TiO_x films deposited on silicon wafers were measured with an ellipsometer (FQTH-100, J.A. Woollam) at a wavelength of 632.9 nm. The TiO_x films were analyzed with FTIR spectroscopy (Nicolet 6700, Thermo Electron Scientific Instruments), and atomic force microscopy (AFM) images were obtained by using a Multimode AFM (Digital Instruments).

Ca corrosion tests were performed by using the method reported in a previous study [12]. In order to carry out a Ca corrosion test, 120 nm thick aluminum layers were deposited on a glass substrate as electrodes. Then, a 250 nm thick Ca layer (20×20 mm^2) was deposited on the glass in partial overlap with the aluminum layers in order to measure the conductance of Ca during oxidation by water vapor. Finally, each Ca-deposited glass sample was encapsulated with a TiO_x film coated onto a PEN or PI substrate by using a UV-cured sealant.

3. Results and discussion

Fig. 1(a) and (b) show the variations with heating time in the refractive indices and film thicknesses respectively of the sol-gel-derived TiO_x films obtained with heat treatments at 45 °C and 110 °C. The refractive indices of the resultant films were found to gradually increase and the film thicknesses to decrease with increases in the heating time. In general, the refractive index and film thickness have close relationships with the film density for oxide thin films. The refractive index, especially, is directly related to the porosity (see supplementary information) [18,19]. These results indicate that the TiO_x films are highly close-packed after heat treatment. It is known that sol-gel-derived TiO_x films are compacted and densified by heat treatments because of the evaporation of small molecules (solvents and by-products) and the polycondensation reactions that occur in TiO_x films. The density of sol-gel-derived films generally depends on the relative rates of evaporation and polycondensation because these events can occur simultaneously when the such films are heated [20]. If the polycondensation reactions occur more rapidly than the evaporation of solvents, the densification of sol-gel-derived TiO_x films can be disturbed by the capture of residual solvents and the formation of pores due to the removal of small molecules (see Fig. 1(c)). As shown in Fig. 1(a), the refractive indices of the TiO_x films are saturated at approximately 1.93 when the films were heated at 110 °C for more than 60 min; this saturation could be due to such restrictions on densification. Therefore, to further improve the density of the TiO_x films, we introduced a two-step heat treatment consisting of a pre-heating step at 45 °C to ensure the evaporation of small molecules and a post-heating step at 110 °C to promote polycondensation reactions.

Fig. 2(a) shows a schematic illustration of the two-step heat treatment. Firstly, the as-spun films were pre-heated at 45 °C for 90 min to induce sufficient solvent evaporation before the TiO_x films are stiffened by polycondensation. The films were then post-heated at a higher temperature (110 °C) for 60 min to promote the polycondensation reactions. Fig. 2(b) plots the variation with the pre-heating time in the refractive index of the TiO_x films after post-heating (110 °C). The refractive index of the TiO_x films increases with increases in the pre-heating time, which means that the pre-heated TiO_x films are more closely packed than those prepared without pre-heating. As a result of the pre-heating step, the