Surface & Coatings Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Water vapor barrier properties of Si–Zn–O/Al multilayer structures

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ARTICLE INFO

Article history:
Received 1 December 2014
Revised 1 May 2015
Accepted in revised form 12 May 2015
Available online xxxx

Keywords:
Water vapor permeation rate
Water vapor barrier
Inorganic/metal multilayer
Magnetron sputtering
Thin films

ABSTRACT

Single-layer Si–Zn–O (SZO) and multilayer SZO/Al films are deposited as water vapor barriers on polyimide (PI) substrates, using magnetron sputtering with SiO_2–ZnO composite and Al targets. The effect of negative substrate bias voltage (V_b) on the microstructure and water vapor barrier properties of the single layer SZO and multilayer SZO/Al films is investigated. The as-deposited SZO film is found by X-ray diffraction analysis to be amorphous. For deposition at $V_b = 0$ V, the SZO film has a columnar structure and rough surface morphology; the Al film exhibits pinholes on the surface. When moderate bias voltages ($V_b = -50$ V for SZO and -70 V for Al films) are applied during deposition, a dense SZO film with smooth surface morphology and a pinhole-free Al film are obtained. An SZO/Al multilayer film shows better water vapor barrier performance than a single-layer SZO, which could be further enhanced by application of V_b to the substrate during film growth.

1. Introduction

In recent years, emerging technologies have employed flexible polymer substrates in devices such as wearable/foldable displays, active radio-frequency identification tags, and integrated circuit smart cards, some of which also need flexible thin film batteries. Recently, a flexible lithium ion battery based on all-solid-state materials, wrapped with polymer sheets, has been reported, which is finally integrated into a flexible display system [1]. Polyimides (PIs) are potential candidates for flexible substrates due to their excellent thermal and mechanical characteristics [2,3]. However, one obstacle to the development of these devices is susceptibility of PIs as well as the devices themselves to water vapor and oxygen in the atmosphere, resulting in reduced device performance. The encapsulation of lithium ion thin-film batteries (LITFBs) is also a major problem because lithium is a very reactive element.

The permeability of polymers to water and gas has been reduced by inorganic coatings, such as Al_2O_3, SiO_2, and SiN_x, on polymer substrates [4–6]. It appears that a high performance gas barrier coating on polymer substrates is indispensable. Gas barrier films have been prepared by various coating technologies, including sputtering [7–10], atomic layer deposition (ALD) [11–13], and plasma-enhanced chemical vapor deposition (PECVD) [14–16]. ALD is known to produce high-performance barrier coatings on various materials as it allows the preparation of dense and pinhole-free inorganic films. However, the ALD technique has some draw backs in its current form due to a time consuming and relatively expensive process [13]. On the other hand, magnetron sputtering is attractive due to the simplicity of the process and the low deposition temperature. Moreover, the sputtering process is compatible with microfabrication techniques for LITFBs. In this study, we prepared a Si–Zn–O/Al multilayer film, which was deposited on PI substrates using RF magnetron sputtering, and investigated the water vapor transmission rate (WVTR). Most of the coatings studied are in the form of single film, but the form of multilayer film such as inorganic layer/metal/inorganic layer may be also promising to create high performance barrier coatings. It has been reported that multilayer stacks exhibit improved barrier properties compared to single layers; some of transparent multilayer barrier coatings on polymer films are reviewed in the recent presentation [17]. However, there is less work reported on the structure and barrier property of the inorganic layer/metal/inorganic layer multilayer coatings prepared by the sputtering method. In the present investigation, a Si–Zn–O/Al multilayer is suggested as one possible barrier coating because aluminium is a very good barrier against water and water vapor.

It is known that in magnetron sputtering, the negative substrate bias voltage (V_b) is a critical deposition parameter; it determines the kinetic bombardment energies of ions arriving on the substrate, which can affect the chemical composition and structure of the as-deposited films [18]. The present study also investigates the effects of V_b on the structure and WVTR of Si–Zn–O/Al multilayer films. As far as we know, the LITFBs are usually fabricated by the sputtering

Abbreviations: SZO, Si–Zn–O; PI, polyimide; ALD, atomic layer deposition; PECVD, plasma-enhanced chemical vapor deposition; WVTR, water vapor transmission rate; XRD, X-ray diffractometry; SEM, scanning electron microscopy; AFM, atomic force microscopy; RMS, root-mean-square.

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http://dx.doi.org/10.1016/j.surfcoat.2015.05.016
0257-8972/

technique and the development of packing materials for flexible LITFBs is a challenging task. The experiments described below are designed with this background in mind.

2. Experimental

Si–Zn–O (SZO)/Al multilayer films were prepared on PI substrates by RF magnetron sputtering at ambient temperature. Layers of Al and SZO were sequentially deposited, using Al metal (purity 99.99%) and SiO_2–ZnO composite (SiO_2 35 mol%/ZnO 65 mol%) targets with a 2 in. diameter, respectively. Prior to deposition, all the substrates were ultrasonically solvent cleaned (10 min isopropyl alcohol and 5 min deionized water successively), and then dried in an oven. SZO films were deposited by reactive sputtering in an Ar and O_2 gas flow (ratio of flow rates: $Ar/O_2 = 6/1$), while Al film was deposited under Ar gas flow. The sputtering chamber was evacuated with a turbomolecular pump down to a base pressure of 3×10^{-6} Torr. The depositions were performed at different negative substrate bias voltages ($V_b = 0$ V, -30 V, -50 V, -70 V, -100 V). The deposition rate was measured with a quartz crystal thickness monitor and film thickness was determined using an Alpha-step 500 (TENCOR) profilometer and cross-section scanning electron microscopy (SEM).

To fabricate the SiO_2–ZnO composite target, the mixture of SiO_2 and ZnO powders was milled in a planetary ball mill (Fritsch GmbH, Germany) for 1 h in air. The milled powder was uniaxially pressed and then sintered at 1100 °C for 2 h in air.

Crystalline structures of the multilayer films and the composite target were characterized by X-ray diffractometry (XRD), using Cu Kα radiation. The surface morphology was analyzed by SEM and atomic force microscopy (AFM). The elemental compositions of SZO films were determined through the energy-dispersive X-ray spectroscopy (EDX). The water vapor transmission rate (WVTR) of samples with a 50×50 mm^2 area was measured using a Permatran-w3/61 model system at atmospheric pressure, 37.8 °C, and 100% relative humidity.

All WVTR values are reported in the unit of g/m^2/day. The measurement of WVTR was done once for the sample obtained under a given deposition condition. In some cases, two pieces of the same sample were measured.

3. Results and discussion

Fig. 1 shows the XRD patterns of the mixture of ZnO/SiO_2 powders and the composite target prepared by sintering the ball-milled mixture

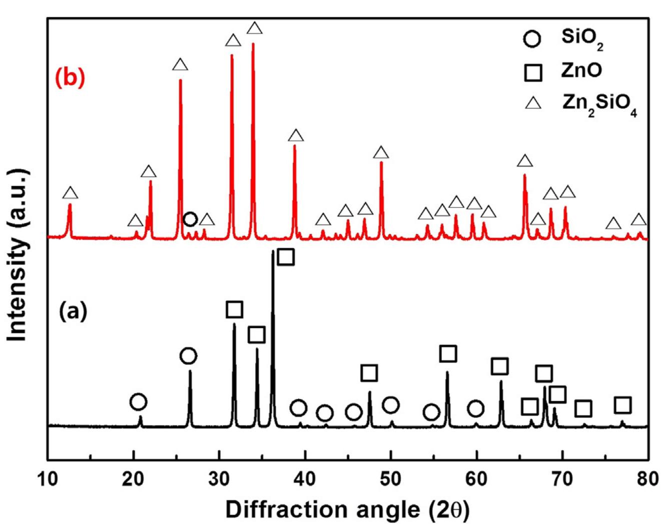

Fig. 1. XRD patterns of (a) the mixture of SiO_2/ZnO powders and (b) the composite sintered target.

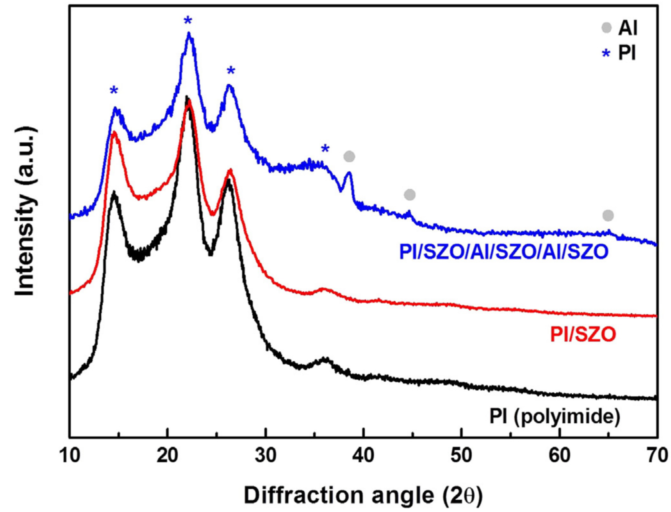

Fig. 2. XRD patterns of the PI/SZO and PI/SZO/Al multilayer films.

at 1100 °C. As a result of sintering, the sputtering target consists of a Zn_2SiO_4 phase and traces of SiO_2. In contrast, for the sputtered SZO/Al multilayer films on PI substrates in Fig. 2, no Zn_2SiO_4 or SiO_2 diffraction peak is observed, showing that the SZO is X-ray amorphous, but crystalline Al peaks appear. The SZO peak is not obvious because of the PI substrate peaks. These structural characteristics of deposited SZO films were confirmed in related tests using SiO_2-coated Si substrates (data not shown here).

Fig. 3 displays AFM images (scanning area was 2 μm × 2 μm) of SZO films coated using different negative substrate bias voltages. Note that the images are representative of the morphologies observed at various scales. The root-mean-square (RMS) surface roughness of SZO films is 2.68, 2.57, and 2.21 nm, corresponding to $V_b = 0$ V, -30 V and -50 V, respectively. However, when the bias magnitude $|V_b|$ is increased further ($V_b = -100$ V), the RMS roughness values increase and the grain size increases. Elemental compositions of the deposited SZO films as a function of V_b are shown in Fig. 4. With increasing $|V_b|$, the atomic content of Si decreases but that of Zn increases, whereas the concentration of oxygen remains around 54.5 at.% as illustrated in Fig. 4(a). As a result, the Si/Zn atomic ratio substantially decreases from 1.34 to 0.7, while the O/(Si + Zn) ratio of all the deposited films is near stoichiometric although it changes slightly as shown in Fig. 4(b). With the compositional changes observed, re-sputtering of the light Si atoms at higher $|V_b|$ may be responsible for the decreased Si/Zn atomic ratio. When a negative bias is applied to the substrate during film deposition, the ions are accelerated by V_b which bombard the surface of the growing film with added momentum and energy transfer. Ion energy will be proportional to $|V_b|$ when other parameters are kept constant during film growth [19]. In consequence, the increasing $|V_b|$ would enhance the re-sputtering of light atoms.

Water vapor transmission rate measurements were carried out for PI/SZO films deposited with different values of V_b. The positive effect of V_b on WVTR is evident in Fig. 5. Among the samples investigated here, the best result is for $V_b = -50$ V. This is supported by the RMS roughness seen in Fig. 3: surface roughness is believed to be a factor affecting WVTR performance, as films with low RMS roughness have good barrier performance [20,21]. However, when $|V_b|$ increases above 50 V, WVTR increases slightly but is still much lower than for film deposited at $V_b = 0$ V, even though RMS roughness is higher. Despite the high roughness, the relatively low WVTR can be attributed to a more densely packed structure with increasing $|V_b|$ [22]. It is also noted that the composition in the SZO film changes with V_b as shown in Fig. 4, but it is not clear at present what effect the compositional change has on WVTR performance. This work is ongoing and will be the topic of a future paper.

Please cite this article as: T.-Y. Kim, et al., Surf. Coat. Technol. (2015), http://dx.doi.org/10.1016/j.surfcoat.2015.05.016