Thin Solid Films 523 (2012) 15–19

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Investigation of chemical bonding states at interface of Zn/organic materials for analysis of early stage of inorganic/organic hybrid multi-layer formation

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ARTICLE INFO

Available online 29 May 2012

Keywords:
Inductively-coupled plasma
Low-inductance antenna
Polymer
Low-damage process
Hard X-ray photoelectron spectroscopy

ABSTRACT

Interactions between Ar–O_2 mixture plasmas and Zn thin film on polyethylene terephthalate (PET) were investigated using the combinatorial plasma process analyzer, on the basis of nondestructive depth analyses of chemical bonding states at Zn thin film and Zn/PET interface via hard X-ray photoelectron spectroscopy (HXPES). After the Ar–O_2 plasma exposure, peak-area ratio of O 1 s to Zn $2p_{3/2}$ evaluated from the HXPES spectra is found to increase with increasing the ion saturation current × time and saturated at the value obtained from ZnO. The HXPES C 1 s spectra measured at a take-off angle (TOA) of 80° showed insignificant change in oxygen functionalities (O=C–O bond and C–O bond) after the deposition of Zn thin film and the plasma exposure. Whereas, the HXPES C 1 s spectra measurement at a TOA of 20° suggested that the oxygen functionalities degraded in shallower regions up to about a few nanometer from the Zn/PET interface due to deposition of Zn thin film. However, after the plasma exposure, oxidation of PET substrate at the degraded layer of Zn/PET interface was caused by oxygen radicals and/or ions, which diffused through the Zn thin film.
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1. Introduction

Inorganic/organic hybrid multi-layer structures are expected as a key structure for the next-generation devices including flexible displays [1], thin-film photovoltaic cells [2] and organic image sensors [3]. For fabrication of the hybrid multi-layer structures, it is significant to form high-quality inorganic layer on organic layer. However, bond-dissociation energies of organic materials for thermal decomposition range from 3.4 eV for the O–C(=O) bond, 3.6 eV for the C–CH_3 bond to 8.4 eV for C=O bond [4]. Thus, in plasma processes, it is considered that ions [5,6], radicals [7,8], photons [9,10] and electrons [11] from the plasma may cause significant degradation of organic layer beneath the surface and/or the inorganic/organic interface. Therefore, it is necessary to develop low-damage and low-temperature formation processes of the high-quality inorganic layer on the organic layer on the basis of understanding interactions between plasmas and materials.

In previous studies, interactions between ions, radicals and photons from Ar–O_2 plasma with organic materials were investigated on the basis of surface morphology and depth analyses of chemical bonding states in the nano-surface layer of organic materials [7,12]. These studies have reported that the Ar–O_2 mixture plasma exposure onto organic materials caused surface etching and oxidation at the nano-surface. These effects of exposure to Ar–O_2 mixture plasmas on organic materials are of significant concern in the formation processes of oxide thin films on organic materials. Therefore, it is important to investigate oxidation behaviors at early stage of oxide thin film formation on organic materials, which is using Ar–O_2 mixture plasmas.

For the investigation of plasma–materials interactions, a plasma process analyzer based on combinatorial methods has been developed [13–16], where by the plasma profiles with density gradient are finely generated with a localized discharge-power deposition using low-inductance antenna (LIA) modules [17]. The plasmas sustained with LIA modules allow high-density plasma production with active control of power deposition profiles and low sheath-edge potential [18–23].

In this study, Zn thin film with a thickness 15 nm was deposited on polyethylene terephthalate (PET) and exposed to Ar–O_2 plasma as a model of early stage of ZnO film formation on organic materials using Ar–O_2 mixture plasma. For analysis of the oxidation behaviors of Zn thin film and Zn/PET interface, the plasma exposure was carried out with the combinatorial plasma process analyzer, which can analyze the plasma-materials interactions efficiently via inclined distribution of process parameters along the substrate [15,16].

In this paper, the interactions between Ar–O_2 mixture plasma and Zn thin film on PET were investigated on the basis of nondestructive depth analyses of chemical bonding states at the Zn thin film and Zn/PET interface via hard X-ray photoelectron spectroscopy (HXPES) [24].

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doi:10.1016/j.tsf.2012.05.061

2. Experimental details

Fig. 1 shows schematic illustration of the combinatorial plasma-process analyzer with two LIA modules. Here it is noted that the unit of the schematic illustration in Fig. 1 is millimeter. The LIA modules ("Antenna 1" and "Antenna 2" in Fig. 1) consisted of a copper tube covered with a quartz tube with a dimension of 70 mm in width and 100 mm in height, and were mounted on the top flange of the chamber [17]. The LIA ("Antenna 1") located perpendicularly to the X axis at $X=260$ mm serves as a main antenna for obtaining major gradation of the plasma density, whereas the LIA ("Antenna 2") located in parallel with the X axis at $X=80$–150 mm serves as sub-antenna to modify the plasma-density distribution along the substrate holder [13]. The LIAs were coupled to independent RF power generators at 13.56 MHz via matching networks. As shown in Fig. 1, the discharge region was surrounded by a T-shaped wall for obtaining gradation of the plasma density [15]. The Ar–O_2 mixture gas was supplied to the discharge chamber through a gas inlet located at the top flange. The Ar–O_2 mixture plasmas were generated at a total pressure of 2.6 Pa with an oxygen partial pressure of 20% in the total pressure via supplying RF power of 175 and 350 W to the main antenna ("Antenna 1"). Previous publication [13] has been reported that steepness of plasma-density is decrease with increasing the RF power of the sub-antenna ("Antenna 2"). Therefore, in order to control the steepness of plasma-density most highly, the RF power of the sub-antenna ("Antenna 2") is kept constant at 0 W.

Ion-saturation current (I_{is}) profiles along the substrate were measured with a cylindrical Langmuir probe located at 5 mm above the substrate. The probe tip made of platinum was used to avoid oxidation.

Zn thin film with a thickness 15 nm was formed on PET substrates using pulsed magnetron sputtering with Ar gas at a pressure of 0.67 Pa. Pulse bias with a frequency of 65 kHz, an average power density of 1.7 W/cm^2 and a duty cycle of 50% was supplied to Zn target. The target–substrate distance was 230 mm. After the deposition process, for investigation of effect of Ar–O_2 mixture plasma exposure on chemical bonding states at Zn thin film and Zn/PET interface, the Zn/PET samples were exposed to the Ar–O_2 mixture plasmas via the combinatorial plasma-process analyzer. Three Zn/PET samples were located at substrate positions $X=40$, 120 and 220 mm. The Zn/PET samples were exposure to the Ar–O_2 mixture plasmas sustained only by the main antenna ("Antenna 1") supplied with RF power of 175 and 350 W for 1052 and 2104 s. Here it is noted that the deposition process of Zn thin film and the Ar–O_2 mixture plasma exposure process were performed using different equipment. Therefore, the Zn/PET samples were exposed to the air before the Ar–O_2 mixture plasma exposure.

Depth analysis of chemical bonding states was carried out with hard X-ray photoelectron spectroscopy (HXPES). The HXPES analysis was performed with hard X-ray from a synchrotron at a photon energy of 7940 eV at the national synchrotron radiation facility SPring-8 of the Japan Synchrotron Radiation Research Institute [24]. The inelastic mean free path of 7940 eV electrons in polymers is approximately 18 nm [25]. Therefore, probing depth of HXPES is about 50 nm for the analysis of polymer [26]. This feature with HXPES makes it possible to evaluate the chemical bonding states in the Zn/PET interface via variation of take-off angle (TOA) for photoelectrons detection from TOA of 80° for the analysis of deeper regions about 35 nm from the interface down to TOA of 20° for the analysis of shallower regions about a few nanometer from the interface.

Here it is noted that the surface of the Zn/PET samples was coated with Pt layer with a thickness of 4 nm prior to the HXPES measurements

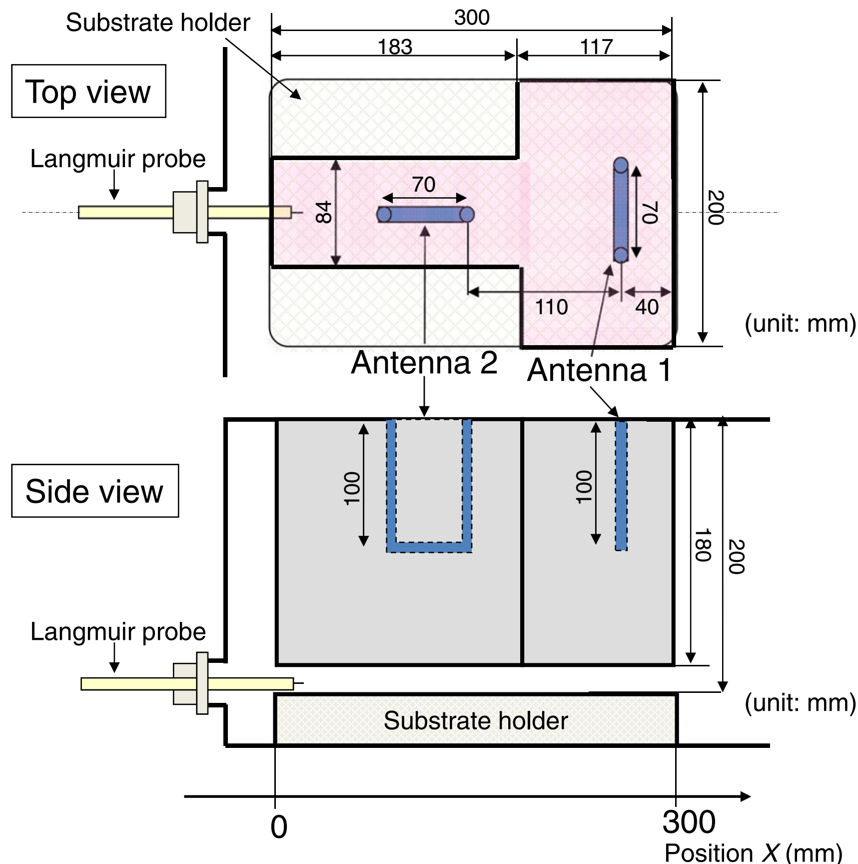

Fig. 1. Schematic illustration of combinatorial plasma-process analyzer with two LIA modules.

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