Materials Science in Semiconductor Processing 89 (2019) 176–185

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Flexible W-doped In_2O_3 films grown on ion beam treated polyethylene terephthalate substrate using roll to roll sputtering

Jae-Hoon Lee, Han-Ki Kim*

School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi 16419, South Korea

ARTICLE INFO

Keywords:
Ion beam treatment
IWO
Roll-to-roll sputtering
Contact angle
Adhesion
Flexible thin film heaters

ABSTRACT

We investigated the effect of Ar ion beam treatment on a polyethylene terephthalate (PET) substrate to grow high-quality flexible W-doped In_2O_3 (IWO) films using a lab-scale roll-to-roll (RTR) sputtering system at room temperature. The electrical, optical, morphological, and mechanical properties of the flexible IWO films sputtered on the ion beam-treated PET and untreated PET substrates were comprehensively compared. In particular, the mechanical flexibility of the RTR sputtered IWO films was investigated in detail using custom-made bending, rolling, and twisting testers. Based on water contact angle and X-ray photoelectron spectroscopy (XPS) measurements, we found that the surface energy change and decreased C-O and C=O groups on the PET substrate led to flexible IWO films with improved adhesion and better mechanical properties. In addition, we compared repeating cooling and heating cyclic stability of the flexible thin film heaters with RTR sputtered IWO films before and after ion beam treatment to show feasibility of ion beam treating process during RTR sputtering.

1. Introduction

Transparent conducting oxide (TCO) thin film coated flexible polymeric substrates are critical components for various flexible optoelectronic devices, such as flexible displays, flexible photovoltaics, flexible and transparent electronics, flexible touch panels, flexible electrochromic devices, flexible energy harvesting devices, and flexible thin film heaters (TFHs) [1–7]. The TCO films coated on flexible substrates have been mainly produced by means of continuous roll-to-roll (RTR) sputtering, which has many commercial merits, including large-area roll-based mass production, a fast coating process, and a low temperature coating process [8,9]. Sn-doped In_2O_3 (ITO) films are mainly used as flexible and transparent electrodes (FTEs) due to their low sheet resistance and high transmittance caused by the degenerated semiconductor properties of ITO films. However, the development of high quality flexible TCO materials to replace conventional ITO films is necessary to overcome the limits of conventional ITO films. Along with several amorphous flexible TCO materials (such as InZnO, InZnSnO, InSiO, and InZnSiO) with high optical transmittance above 80% only in a visible region, W-doped In_2O_3 (IWO) films have attracted interest as promising high mobility TCO electrodes due to their high carrier mobility and high transmittance in the visible and infra-red (NIR) wavelength region [10–15]. As noted in the review by Calnan et al., transition metal dopants such as W, Mo, Ti, Nb, and Ta with high Lewis acid strength (LAS) values led to a reduction in scattering and increasing the carrier mobility [16–21]. In our previous work, we also reported the potential of high mobility IWO films on glass substrates for organic solar cells [22]. Although the electrical and optical properties of sputtered IWO films are well reported, an investigation of flexible IWO films prepared by a room temperature RTR sputtering process is still lacking [23–29]. For high-quality flexible optoelectronic devices, the flexible IWO films must have good adhesion between the IWO film and polyethylene terephthalate (PET) substrate because the surface of a typical PET substrate is innately hydrophobic, has low surface energy and shows high chemical inertness [30–33]. For these reasons, the modification of the PET surfaces is necessary before RTR sputtering of flexible TCO films to increase the wettability and the surface energy. Several surface treatment methods have been reported for polymeric substrates such as photo-activation, corona treatment, laser treatment, plasma treatment and ion irradiation [34–36]. In particular, linear ion beam treatment has been employed as an effective pre-treatment process to enhance wettability on a flexible PET substrate in the RTR sputtering system [37,38]. Ion beam irradiation promotes interactions between ionized particles and a polymeric substrate in elastic/inelastic collisions, thus producing different phenomena such as chains scission, sputtering evaporation, carbonization, ionization and free radicals, which can produce important surface chemical changes [39–44]. However, there is no report on linear ion beam treatment effects for

* Corresponding author.
E-mail address: hankikim@skku.edu (H.-K. Kim).

https://doi.org/10.1016/j.mssp.2018.09.015
Received 1 August 2018; Received in revised form 6 September 2018; Accepted 16 September 2018
1369-8001/

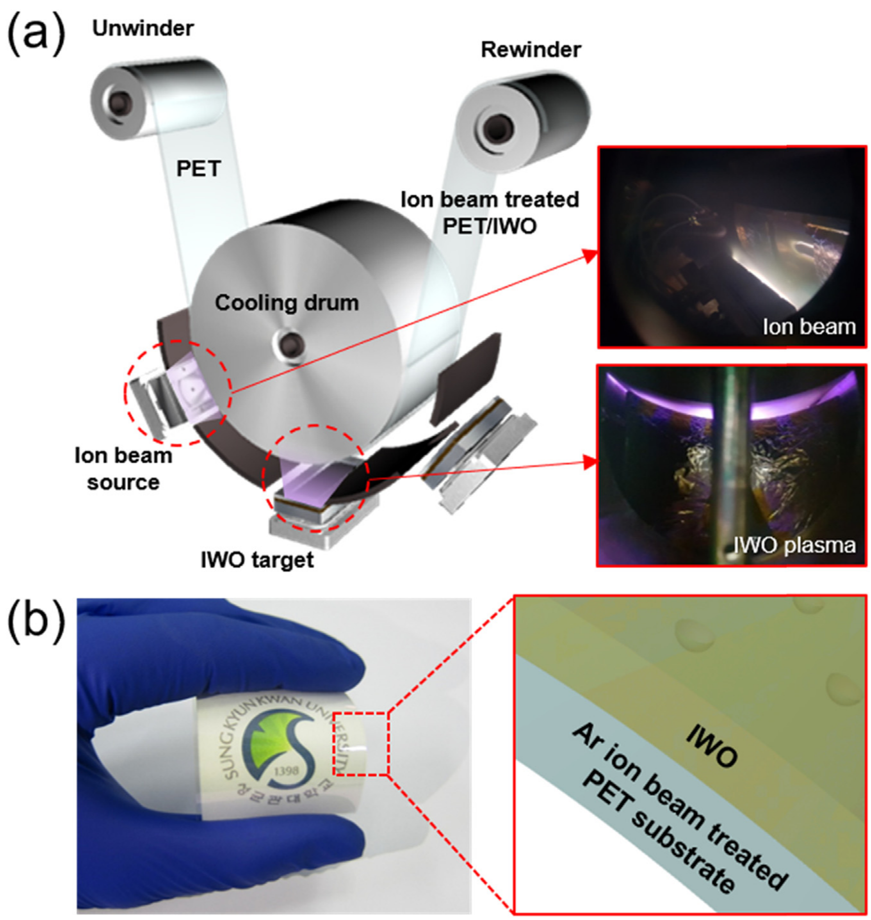

Fig. 1. (a) Schematic drawing of a lab-designed RTR sputtering system with a linear ion beam source and rectangular cathode. (Right) Pictures show Ar ion beam irradiated on PET substrate and plasma on the IWO target. (b) Photograph of optimized RTR sputtered IWO film on Ar ion beam treated PET substrate and enlarged schematic structure of the IWO/PET sample.

PET substrate to obtain high-quality flexible IWO films using the RTR sputtering process.

In this work, we examined the effect of Ar ion beam treatment on a PET substrate to grow high quality flexible IWO electrodes using a lab-scale RTR sputtering system. Electrical, optical, morphological and mechanical properties of flexible IWO films sputtered on the ion beam-treated PET and untreated PET substrates were compared in detail. We compared surface energy changes and surface chemical binding of the PET substrate before and after ion beam treatment using water contact angle measurements and X-ray photoelectron spectroscopy (XPS). In addition, we fabricated typical TFHs and compared the performance of the TFHs with flexible IWO electrodes sputtered on ion-beam treated and untreated PET substrates.

2. Experimental

Flexible IWO films were prepared on a commercial PET substrate with a width of 150 mm using the lab-scale RTR sputtering system (SNTEK RTR2006). Fig. 1(a) shows a schematic of the lab-scale RTR sputtering system equipped with an unwind roller, rewind roller, cooling drum, and linear ion beam system. The pictures on the right in Fig. 1(a) demonstrate Ar ion beam and plasma on the IWO target during the continuous RTR sputtering process. As illustrated in Fig. 1(a), the 150 mm wide PET substrate was passed over a linear ion beam source and an IWO target via the motion of unwind and rewind roller. The ion beam source was placed at a distance of 100 mm from the PET substrate, and the Ar ion beam incidence angle was 90°. Prior to IWO sputtering, the surface of the PET substrate was treated by Ar ion beam irradiation as a function of working pressure and DC power to optimize the ion beam treatment conditions. Then, the 150 nm-thick IWO film was directly sputtered on the ion beam treated PET substrate using a rectangular IWO target (1 wt% WO_3-doped In_2O_3, DASOM RMS) at a fixed Ar:O_2 gas flow ratio of 30:1 sccm, a working pressure of 1 mTorr, a DC pulsed power of 550 W, and a rolling speed of 1.12 cm/sec. Fig. 1(b) shows the optimized flexible IWO film on an Ar ion beam treated PET substrate with a size of $25 \times 25\ mm^2$ before fabrication of flexible TFHs. The wettability and total surface energy of PET substrates before and after ion beam treated were investigated by the water contact angle measurements (Phoenix-MT(A), SEO) using two different liquids, i.e., deionized water and diiodomethane which had a constant volume of 3 ml. XPS (K-Alpha, Thermo Electron) analysis were employed to compare the change of peak intensities at the binding energies of the untreated and Ar ion beam treated PET substrates. The electrical properties and optical properties of flexible IWO films sputtered on the Ar ion beam treated and untreated PET substrate were measured by the Hall measurements (HL5500PC, Accent Optical Technology) with operating current of 5 mA and were examined in a range of wavelength 340–1200 nm by UV/Vis spectrometer (V-670, Jasco), respectively. The mechanical properties of the IWO films were evaluated based on various bending test modes, such as outer and inner bending, rolling, and twisting tests. In addition, dynamic fatigue bending, rolling and twisting tests were performed at frequencies of 1 Hz for 10,000 cycles. A change in resistance for each IWO film due to substrate bending can be expressed as $\Delta R = (R-R_0)/R_0$, where R is the in-situ measured resistance under substrate bending and R_0 is the initial measured resistance. Furthermore, a field emission scanning electron microscope (FESEM: MERLIN, Carl Zeiss) with operating voltage of 5 kV was used to observe the surface morphologies of the IWO films sputtered on untreated and Ar ion beam treated PET substrates before and after bending tests. To demonstrate the feasibility of using flexible IWO films sputtered on Ar ion beam treated PET substrates, flexible TFHs were fabricated on the RTR sputtered IWO electrode with