Applied Surface Science 259 (2012) 582–589

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Reactive sputtering of ZnO:Al thin films from rotatable dual metallic targets

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ARTICLE INFO

Article history:
Received 15 April 2012
Accepted 5 July 2012
Available online 25 July 2012

Keywords:
ZnO:Al thin film
Reactive sputtering
PEM intensity
Oxygen partial pressure

ABSTRACT

In this study, aluminum doped zinc oxide (ZnO:Al) films were prepared by reactively sputtering from rotatable dual metallic targets, which were controlled by a plasma emission monitoring (PEM) system. The influences of different sputtering conditions including different discharge powers, working pressures and working points (or oxygen partial pressure) on ZnO:Al films are investigated systematically. It is found that the deposition rate strongly relies on the discharge power. However, different PEM intensities lead to different deposition rates, which are related with oxygen partial pressure as well as the sputtering properties to oxide (ZnO) and metal (zinc) materials. In addition, the oxygen partial pressure at different PEM intensities strongly influences the electrical and optical properties as well as morphologies and etching behaviors of ZnO:Al films. High rate ZnO:Al films with good electrical and optical properties as well as proper surface structures are achieved at the transition mode region. High deposition rate of up to 100 nm m/min and high carrier mobility of up to 41 cm^2/Vs are achieved, which demonstrates the great advantage for such a cost-efficient sputtering technique. The surface structure of high rate ZnO:Al films can be modified further by etching with a novel two-step etching method and good device performance has been achieved when they applied in silicon thin film solar cells.

1. Introduction

High efficiency silicon thin film solar cells strongly rely on light scattering typically introduced by rough TCO front contacts [1–4]. Sputter deposited and texture etched aluminum doped zinc oxide (ZnO:Al) films with optimized surface structures could supply a good light trapping effect to improve the short circuit current (J_{sc}) [5–7]. In the past, the ZnO:Al films were prepared by sputtering from planar or tube ceramic targets [8,9]. Recently, ZnO:Al films with quite good quality were achieved through a reactive magnetron sputtering technology [10–14]. The reactive sputtering was stably carried out in a non-stable transition mode region using a closed loop control system by adjusting the discharge power according to the measured oxygen partial pressure (Po_2) by a λ-sensor. Moreover, they can increase the target utilization by moving the magnetron behind the targets. Hüpkes et al. [13,14] also studied reactive magnetron sputtering of ZnO:Al films from planar targets at a mid-frequency of 40 kHz systematically. They also achieved good ZnO:Al films with good electrical and optical properties as well as good surface structures in the transition mode region. However, the sputtering process was controlled by a plasma emission monitoring (PEM) system, which controls the deposition stably carrying out at different working points in the transition mode region by adjusting the oxygen gas flow (Fo_2) according to the setting PEM intensity. Similar to the non-reactive sputtering technique from tube (rotatable) ceramic targets, the tube metallic targets are used for preparation of ZnO:Al films in reactive sputtering technique [15,16]. Such a sputtering technique could greatly increase the deposition rate and in the mean while enhances the utilization of target material (over 80%). As a result, the production cost could be greatly reduced and thus it attracts a great of attention of a lot of researchers recently.

In this study, ZnO:Al films were reactively sputtered on corning glasses in a vertical in-line rotatable dual magnetron sputtering (RDM) system, which is similar to non-reactive sputtering deposition system [17]. Differently, the PEM system was incorporated into this sputtering system to monitor and control reactive sputtering process mentioned above. The influence of different discharge powers and working points with different oxygen partial pressures on ZnO:Al films are systematically investigated.

2. Experimental details

ZnO:Al films were reactively sputtered on glass substrates (Corning, Eagle XG) in a vertical in-line sputtering system (VISS 300, by von Ardenne Anlagentechnik, Dresden, Germany). Rotatable dual magnetron cathodes (RDM) with metallic Zn:Al tube targets (0.5 wt%) were operated at discharge powers between 4 kW and

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0169-4332/$ – see front matter.
http://dx.doi.org/10.1016/j.apsusc.2012.07.080

Table 1
Different series of reactive sputtering depositions (set A, B, C, D and E) at different deposition conditions (discharge power, opening percent of throttle valves, PEM intensity, substrate temperature and inputted argon gas flow).

	Discharge power (kW)	Opening percent of throttle (%)	Substrate temperature (°C)	Argon gas flow (sccm)	PEM intensity (%)
Set A	4	65%	300	200	10, 20, 25, 30, 35, 40, 50
Set B	4	60%	300	200	25, 30, 35, 40
Set C	8	60%	300	200	20, 25, 30, 35, 40, 50
Set D	10	60%	300	200	20, 25, 30, 35, 40, 50
Set E	10	50%	300	200	25, 30, 35, 40, 50

10 kW with mid-frequency excitation of 40 kHz. The target sizes are 760 mm in length and 160 mm in diameter. Approximate 10 mm thick target material was bonded on the metallic tube. The argon gas flow and substrate temperature were 200 sccm and 300 °C, respectively. During the reactive sputtering process, the oxygen gas flow Fo_2 was controlled by PEM system according to set intensity of 307 nm zinc emission line, which was used to characterize the process for different working points. The working point or PEM intensity was set from 10% to 50%. The corresponding deposition mode varies from oxide mode to transition mode to metallic mode with the increasing PEM intensity from 10% to 50% in this study. The main working pressure was controlled by changing the opening percent of throttle valve for example 60% or 65%. However, the practice working pressure will vary with the change of PEM intensity, which is mainly due to a different input of oxygen gas flow controlled by PEM system. In this study, we focus on the sputtering depositions of ZnO:Al films under various deposition condition sets. Based on these deposition conditions, we define them as set A–E as shown in Table 1. During the dynamic sputtering, the glass substrate oscillates in front of the rotatable dual ceramic targets. More details about PEM control and sputtering process can be found in literatures [13,16,18]. As-grown ZnO:Al films were etched in aqueous solutions of diluted hydrochloric (HCl 0.5%) to get a textured surface for further application in silicon thin film solar cells.

The thickness of ZnO:Al films was measured with surface profiler. The electrical properties of the films were investigated by Hall effect measurement using van der Pauw method. Optical properties of the as-grown and surface textured ZnO:Al films including total transmission (TT), reflection and diffuse transmission (DR) were carried out with a double-beam spectrometer equipped with an integrating sphere (Perkin Elmer Lambda 19). The index matching fluid (CH_2I_2) was used to avoid systematic measurement errors due to light scattering of the rough films during optical measurement for absorption determination [19]. The topographies of all films were investigated by scanning electron microscopy (SEM, Supra 55VP SmartSEMTM, Carl Zeiss, Germany). The chemical compositions of sputtered ZnO:Al films were characterized by secondary ion mass spectroscopy (SIMS).

3. Results and discussions

Fig. 1 shows an example of test curves about the relationships between oxygen gas flow (Fo_2) and PEM intensity at a low and a high discharge powers (4 kW and 10 kW). Hüpkes et al. [13] and May et al. [18] reported more details about these relationships from experiment results. We define the high PEM intensity region as Metallic mode region, low PEM intensity as Oxide mode region. Between them, it is the transition region as shown in Fig. 1(a). The hysteresis region at low discharge power, which is enclosed by opening circle dash lines in Fig. 1(a), is narrower than that at high discharge power. It indicates that at a higher discharge the oxygen gas flow Fo_2 varies much stronger when the sputtering deposition at different working points along the S-curve (solid sphere dash line) than that at a lower discharge. This is also reflected in the variation extent of oxygen partial pressure Po_2 as shown in Fig. 1(b). In addition, the Po_2 increases from metallic mode region to oxide mode region, which goes along the S-curve from bottom points to top points (solid sphere dash line) shown in Fig. 1(b). Furthermore, it can be deduced that the same working point for example 35% will slightly shift toward low oxygen gas flow when the main working pressure increases or the opening percent of throttle valve decreases. The oxygen partial pressure will slightly increase with the enhanced working pressure. More details about theoretic analysis can be found in literatures [20,21] and the following experimental results will prove such a deduction.

For the ZnO:Al films deposited at the same deposition condition group, they show close working pressures as shown in Fig. 2(a). In addition, a higher opening of throttle valve shows a lower working pressure. For example, the films deposited under deposition condition group set A with 65% openings of throttle show a lower working pressure of approximate 0.7 Pa while the films deposited under

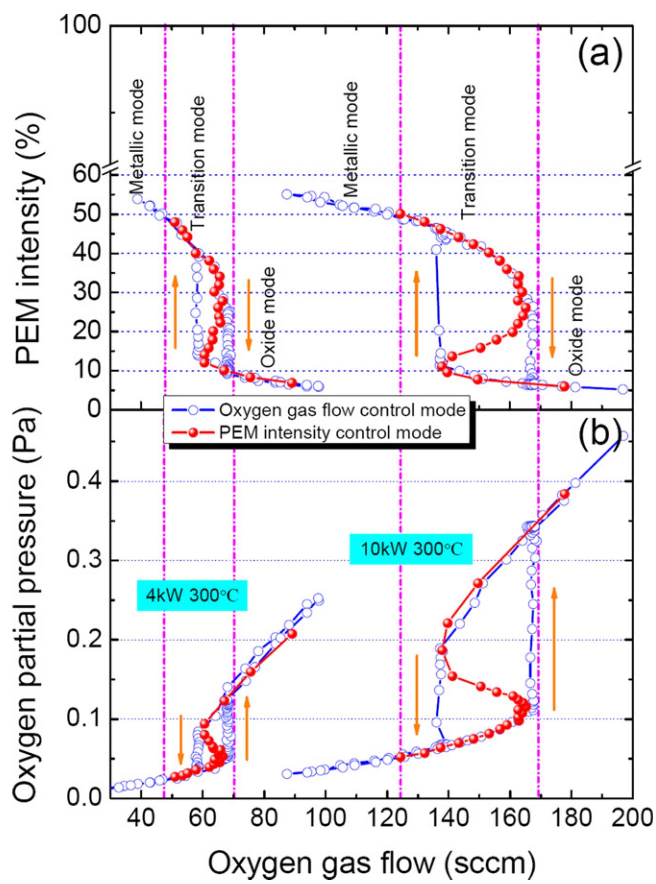

Fig. 1. Dependence of PEM intensity of emitted zinc line (307 nm) (a) and oxygen partial pressure (b) on oxygen gas flow for low rate and high rate reactive sputtering of ZnO:Al thin films from zinc metallic targets under 4 kW and 10 kW, respectively. The sputtering could happen at three reactive regions-metallic mode region, oxide mode region and transition mode region. For sputtering at transition region, it has to be controlled by PEM system due to the instability of reactive sputtering as denoted with solid sphere symbol.