Thin Solid Films 555 (2014) 48–52

Contents lists available at ScienceDirect

Thin Solid Films

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

Damp heat stable doped zinc oxide films

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ARTICLE INFO

Available online 13 August 2013

Keywords:
Zinc oxide
Electrical properties
Thermal treatment
Damp heat stability

ABSTRACT

Zinc oxide is widely used as transparent contact in thin film solar cells. We investigate the damp heat stability of aluminum doped ZnO (ZnO:Al) films sputter deposited at different conditions. Increase in resistivity upon damp heat exposure was observed for as-deposited ZnO:Al films and the water penetration was directly linked to this degradation. Deuterium was used as isotopic marker to identify the amount of water taken up by the films. Finally, we applied a special annealing step to prepare highly stable ZnO:Al films with charge carrier mobility of 70 cm^2/Vs after 1000 h of damp heat treatment. A grain boundary reconstruction model is proposed to explain the high stability of ZnO:Al films after annealing.

1. Introduction

Optoelectronic devices like thin film solar cells rely on a transparent conductive oxide (TCO) to act as a window layer and provide electrical contact [1–3]. As one such TCO, doped zinc oxide has received much attention [2,4,5]. A variety of deposition techniques is utilized to produce doped zinc oxide thin films (ZnO), such as sol gel coating [6], chemical vapor deposition (CVD) [2,7], and sputter deposition [8–11]. Sputter deposition of aluminum doped zinc oxide (ZnO:Al) is an industrial process to coat large area glass sheets. Recently, treatments have been reported to improve the charge carrier mobility of ZnO films [12,13]. Highest mobilities of up to 70 cm^2/Vs at charge carrier density of about 5×10^{20} cm^{-3} have been achieved for sputtered ZnO:Al films after high temperature treatment under a protective silicon layer [14].

The long-term electrical stability of ZnO is a critical issue for application [15–17] and a better understanding of possible degradation processes appears imperative. ZnO is not the most stable form of zinc compounds under environmental conditions, zinc oxide is quite sensitive to aqueous solutions [3,18–23] and most zinc is mined in the form of sulphides, carbonates and hydrocarbonates [24]. During normal operation devices might be encapsulated to minimize detrimental effects of the environment [25]. Nevertheless the stability of bare, unencapsulated devices or coatings is considered an important lifetime limiting parameter. To obtain information on long term outdoor stability devices or coatings are exposed to elevated temperature in a humid environment, so called damp heat treatments [16,21,25–28]. Depending on the ZnO preparation technique used, different degradation results were observed and, for example, the roughness of the underlying substrate was found to influences the rate of degradation strongly [16]. It has been noted that in general, growth conditions which yield dense films offer better stability [17,29]. However, the fundamental mechanism of degradation in ZnO:Al is still not well understood.

Several attempts have been followed to improve the stability of ZnO films in humid environments. Development of special preparation conditions of the ZnO films lead to quite stable material [17,25,30]. More effectively, special protective coatings have been applied to avoid penetration of environmental species during exposure [31,32]. However, the degradation of the electrical properties upon damp heat treatments is slowed down only, rather than being stopped.

To better understand this degradation process, we investigated the accelerated degradation of ZnO:Al in a damp-heat environment using water (H_2O), as well as, deuterated water (D_2O). The D_2O was used as a marker for Secondary Ion Mass Spectrometry (SIMS) measurements to distinguish between hydrogen incorporated during or just after deposition from the atmosphere on the one hand and on the other hand the deuterium incorporated during the damp heat treatment. Finally, we demonstrate highly stable ZnO:Al films, which are highly conductive even after 1000 hours of damp heat treatment. This stability coincides with the reduced water penetration of the ZnO:Al film.

2. Experimental details

All ZnO:Al films were prepared on cleaned (10×10) cm^2 glass substrates (Corning Eagle XG) using radio frequency (RF, 13.56 MHz) magnetron sputtering from planar ceramic targets $(100 \times 750$ $mm^2)$ in dynamic deposition mode. Two types of polycrystalline ZnO:Al films have been investigated, one usually used for silicon based thin film solar cells (referred to as Si–ZnO:Al) [33] and the second one

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http://dx.doi.org/10.1016/j.tsf.2013.08.011

relevant for chalcopyrite solar cells (referred to as CIGS-ZnO:Al) [29]. Details on the processes and material properties can be found in the respective literature. The Si-ZnO:Al was sputter deposited in a vertical in-line system (VISS 300, von Ardenne Anlagentechnik GmbH, Dresden, Germany) from a ceramic target consisting of ZnO with 1 w/w% Al_2O_3. The deposition was carried out at a heater temperature of 420 °C, a discharge power density of 2 W cm^{-2}, and an Ar pressure of 0.1 Pa. The target to substrate distance was 8 cm. The CIGS-ZnO:Al films were sputtered in a nearly identical system at discharge power density of 3.3 W cm^{-2}, an Ar pressure of 0.15 Pa, and heater temperature of 275 °C from ceramic target with 2 w/w% Al_2O_3. Deposition times were adjusted to achieve thickness of 770 nm–870 nm for all Si-ZnO:Al and CIGS-ZnO:Al films.

After ZnO:Al sputtering a special heat treatment under a protective silicon layer was performed to improve the electrical properties [12]. The protective silicon layer of about 50 nm thickness was deposited by plasma enhanced chemical vapor deposition at conditions that are commonly used for the preparation of the doped layers of silicon thin film solar cells. The silicon was prepared in a parallel plate reactor for 10×10 cm^2 substrates at 190 °C heater temperature, gas flows of 69 sccm SiH_4, 100 sccm H_2, 1 sccm PH_3, deposition pressure of 160 Pa, and 4 W RF power (13.56 MHz). In an evacuated tube oven we annealed the ZnO:Al films at 650 °C for 24 hours plateau time with heating and cooling rates of 14 K/min and 1.4 K/min, respectively. After annealing the silicon capping layer was removed by NF_3 plasma etching, as used for chamber cleaning of plasma enhanced chemical vapor deposition reactors [34]. With the very selective plasma process we etched the silicon three times longer than we would expect to be required from etch rates and still did not observe any effects to the ZnO:Al films. This prolonged etching has been performed to be sure all silicon is removed. This heat treatment under the protective silicon layer is known as “high mobility annealing” of ZnO:Al [35]. All annealing steps leading to high mobility mentioned in the paper refer to the heat treatments including removal of the protective layer as just described.

The as-deposited, as well as, capped, annealed, and decapped ZnO:Al films were then exposed to a damp heat treatment for 1000 hours in a climatic chamber at standard conditions (85 °C, 85% humidity). Alternatively, we used Deuterium as an isotopic marker. For this we placed a glass exsiccator with a few drops of deuterated (D_2O) or normal water in an oven set to 95 °C, and a built-in thermometer measuring near the exsiccator registered approximately 88 °C. Following the damp heat degradation, electrical properties were analysed by Hall effect measurements using van der Pauw geometry. All provided charge carrier concentration and mobility values are related to electrons in the n-type semiconductor ZnO:Al. As measure for water penetration we determined the deuterium concentration using secondary ion mass spectroscopy (SIMS, Quadrupol-SIMS apparatus: ATOMIKA — model 4000). Cs ions with 6 keV at 45° incidence sputtered the material and we detected negative secondary ions.

3. Results

Fig. 1 shows resistivity (a), charge carrier mobility (b) and density (c) of Si-ZnO:Al films after damp heat degradation in the exsiccator. A linear increase in resistivity over time was observed, which was caused mainly by a degradation of the mobility. As reference, a heat only treatment is shown (green triangles), where only quite small influence on electrical properties was detected. These ZnO:Al films were placed next to the exsiccator in the oven. The damp heat experiments distinguish between water (H_2O, blue squares) and D_2O (red circles) treatment. There are some variations in the exact resistivity and mobility values for nominally identical experiments, as seen in the open and closed symbols, but all films degraded by this damp heat treatment in a similar manner. The slight differences in the experimental results, e.g. the blue open symbols (H_2O) and the black closed symbols (D_2O), are much smaller than the effects observed in the repeated damp heat treatments with the same type of water (compare open and closed blue symbols for H_2O). The type of water did not alter the degradation effect on ZnO:Al properties severely and we assume the same mechanism behind the degradation for H_2O and D_2O treatments. To test this, we extended the treatment of D_2O degraded samples after 304 h to 1000 h by applying a subsequent H_2O treatment (black squares). In this case the total treatment time is given and the ongoing degradation supports our previous statement.

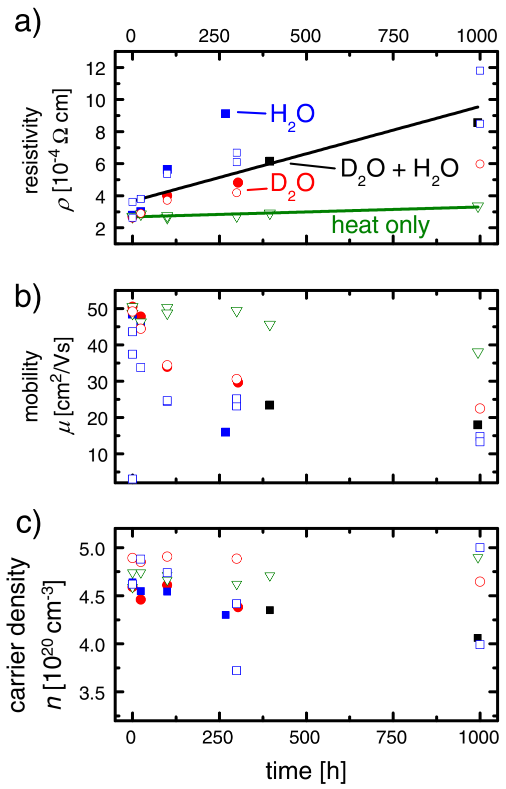

Fig. 1. Resistivity, charge carrier mobility and density of Si–ZnO:Al films as function of treatment time. The exsiccator damp heat in H_2O (blue squares), D_2O (red circles), and H_2O-treatment after 304 h D_2O treatment (black squares) and heat-only (green triangles) as reference treatments were applied. The open and closed symbols correspond to nominally identical conditions, but samples were separately treated. The solid guide-to-the-eye lines indicate the nearly stable (green) and increasing (black) resistance for the heat-only treatment and the ensemble of all damp heat treated ZnO:Al films, respectively.

The deuterium content in the Si-ZnO:Al films is shown as depth profile in Fig. 2. The as-deposited ZnO:Al film serves as reference with the usual hydrogen content just from deposition with the natural Deuterium fraction. After D_2O treatment the D content increases gradually throughout the entire film. Even close to the substrate interface a remarkable increase in D content is visible. Close to the surface of the ZnO:Al films we observed a strong D signal and after the surface accumulation layer the signal decreased towards the substrate interface.

Fig. 3 shows the integration of the D contents shown in Fig. 2 as a function of damp heat exposure time. A linear increase was observed with a slope of $(2 \pm 1) \times 10^{12}$ D atoms per hour for a D_2O treatment (red circles). Even after 1000 h saturation in water penetration did not occur. The ZnO:Al film treated for 304 h in D_2O (series of solid red circles) was then placed into an additional H_2O treatment. The further damp heat process with H_2O (black squares) replaced a large amount of the Deuterium immediately, about 74% and 84% after 24 h and after about 700 h, respectively.

To improve the electrical performance of the ZnO:Al films we performed the high mobility annealing treatment [12,35] under a silicon protection layer. This annealing resulted in high charge carrier