Materials Science in Semiconductor Processing 56 (2016) 302–306

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Influence of vacuum and Ar/CdS atmospheres-rapid thermal annealing (RTA) on the properties of Cd_2SnO_4 thin films obtained by sol-gel technique

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ARTICLE INFO

Keywords:
Cadmium tin oxide
Thin films
Sol-gel
Rapid thermal annealing

ABSTRACT

Transparent conducting oxides are electrical conductive materials with low absorption of light. In recent years, considerable attention has been paid to ternary oxides such as $CdIn_2O_4$, Zn_2SnO_4, $ZnGa_2O_4$, and Cd_2SnO_4. In present work, Cd_2SnO_4 thin films were deposited via dip-coating; dipping solution was synthesized by sol-gel technique from the mixture of CdO and SnO_2 precursor solutions. The films were obtained with 7 layers (~260 nm) on Corning glass substrates. Each coating was deposited at a withdrawal speed of 2 cm/min, dried at 100 °C for 1 h, and then sintered at 550 °C for 1 h in air. The films were subjected to rapid thermal annealing (RTA) treatments at an annealing temperature of 600 °C for 5 s, under two different atmospheres: vacuum and Ar/CdS (varying Ar pressure inside the chamber from 50 to 200 Torr). X-Ray diffraction patterns showed that all the annealed films were constituted mainly by Cd_2SnO_4 crystals with a very low presence of $CdSnO_3$. All the films showed a high optical transmittance (above 80%) in the UV–Vis region. A slight decrease of transmittance occurs in the near infrared region for RTA films, but it is not as pronounced as the one observed when these films are treated using conventional annealing. The minimum resistivity value obtained was 2.87×10^{-3} Ω cm (1.1×10^{2} Ω/□) corresponding to RTA films in vacuum. Electrical and optical properties of the films analyzed in present study make them attractive as electrodes for solar cells, with the advantage of requiring very short annealing times.

1. Introduction

Transparent conducting oxides (TCOs) are electrical conductive materials with low absorption of light. The way to obtain good transparent conductors (transmission higher than 80% and electrical resistivity about 10^{-3} Ω cm or less) is to create electron degeneracy in a wide band gap (greater than 3 eV) oxide by introducing non-stoichiometry and/or appropriate dopants. These conditions are attained in thin film TCOs. Bädeker obtained the first TCO in 1907 by thermal oxidation of sputtered cadmium films [1]. Multiple electronic and optoelectronic applications based on transparent conductors have raised, some of them include: resistors, electrodes in solar cells, flat panel displays, heat-reflecting mirrors, selective absorber components in solar heat collectors, gas sensors, etc. The most commonly used TCOs are SnO_2, ZnO, and In_2O_3:Sn, which have been widely investigated. In recent years, considerable attention has been paid to ternary oxides such as $CdIn_2O_4$ [2], Zn_2SnO_4 [3,4], $ZnGa_2O_4$ [5,6], and Cd_2SnO_4 (CTO) [7,8]. CTO in film form is an n-type semiconductor with high transmittance and high reflectance in the infrared region, and is remarkably stable [9]; it was implemented in the record setting efficiency for CdTe cells reported in 2004 (16.5%) [10]. Nozik carried out one of the earliest studies on the preparation of CTO layers; reporting an electronic mobility of 100 cm^2/V s at a carrier concentration of 5×10^{18} cm^{-3} [11].

Different techniques have been applied for the preparation of CTO thin films. An increasing number of studies report the use of conventional thermal treatments after deposition using atmospheres such as air, Ar [12], He [13], N_2 [9], vacuum [14], Ar/CdS [15,16], with the purpose of improving CTO electrical properties. As far as we know, the resistivity of 1.28×10^{-4} Ω cm is the lowest reported for any CTO film; Wu et al. prepared a polycrystalline film by radio frequency magnetron sputtering, subsequently exposing it to an Ar/CdS anneal at 680 °C

Abbreviations: RTA, rapid thermal annealing; TCO, transparent conducting oxide; CTO, cadmium tin oxide; Ta, annealing temperature; CVA, conventional vacuum annealing; Ts, sintering temperature; t_T, treatment time; XRD, X-ray diffraction; MDI, Materials Data Incorporated; UV–vis–NIR, ultraviolet–visible–near infrared; NA, without annealing treatment; CA, conventional annealing

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http://dx.doi.org/10.1016/j.mssp.2016.09.017
Received 12 May 2016; Received in revised form 15 August 2016; Accepted 14 September 2016

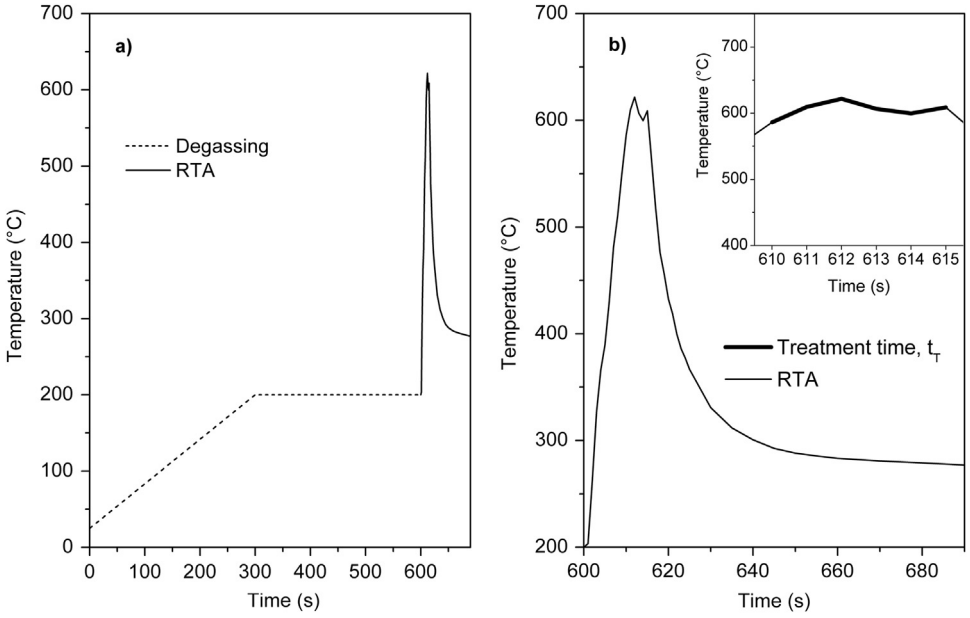

Fig. 1. Representative curve of a) RTA including previous degassing stage, b) RTA process highlighting treatment time, t_T.

[17]. Besides, in the study developed by Diliegros et al. [16], the minimum resistivity obtained was ~4×10^{-4} Ω cm (R_{sheet}=20 Ω/□) corresponding to films synthetized by sol-gel dip-coating on quartz and conventionally treated at an annealing temperature (Ta) of 600 °C under an Ar/CdS atmosphere. In the same study, a minimum value of $\rho=1.8\times10^{-3}$ Ω cm was measured in CTO films exposed to conventional vacuum annealing (CVA). Moreover, resistivity of films deposited on glass and only sintered in air at the sintering temperature (Ts) of 550 °C was equal to 2.1×10^{-2} Ω cm, which is not an adequate value for their use as a TCO [16].

In present work, Cd_2SnO_4 thin films were deposited via dip-coating. Dipping solution was synthesized by sol-gel technique from the mixture of CdO and SnO_2 precursor solutions. The films were sintered at Ts=550 °C for 1 h in air. Afterwards, they were subjected to rapid thermal annealing (RTA) treatments at a Ta=600 °C under two different atmospheres, vacuum and Ar/CdS. Several publications report the use of RTA on different materials, such as transparent oxides [18–26], organic solar cells electrodes [27,28], photovoltaic absorber layers [29], silicon films [30], diverse semiconductors [31–33], graphene oxide [34]; among others. It is our knowledge that there are not previous studies about the effect of post-deposition RTA on Cd_2SnO_4 thin films properties.

2. Experimental details

2.1. Cd_2SnO_4 films

CTO films were deposited via multiple-dipping method. The dipping solution was synthesized by sol-gel technique from the mixture of CdO and SnO_2 precursor solutions, obtained independently. Both solutions were mixed at room temperature, in order to get a final tin atomic concentration percentage in solution of 29 at%. The cadmium oxide precursor solution was prepared using cadmium acetate ($(CH_3COO)_2Cd{\cdot}2H_2O$) (1 mol), methanol (33 mol), glycerol (0.2 mol), and triethylamine (0.5 mol) [35]. The tin oxide precursor solution synthesis was performed according to the procedure previously reported [36], with a change in the molar concentration of trimethylamine. This solution was prepared starting from stannous chloride ($SnCl_2{\cdot}2H_2O$) (1 mol), ethanol (40 mol), glycerol (0.20 mol), and triethylamine (0.10 mol). As stated by Diliegros et al. [37], lactic acid (0.4 mol) was added to the mixture of both solutions in order to obtain a transparent final precursor solution.

The films were deposited on commercial glass substrates (Corning 2947) and were constituted of seven layers (~260 nm). Each coating was deposited at a withdrawal speed of 2 cm/min, dried at 100 °C, and then sintered at 550 °C, in both cases in air atmosphere for 1 h. Afterwards, a set of films was exposed to thermal treatment in a RTA system, under vacuum atmosphere at Ta=600 °C with a treatment time (t_T) of 5 s. On the other hand, a set of films was subjected to RTA using the same Ta and t_T under an atmosphere of Ar with CdS vapor (Ar/CdS), at different Ar pressures inside the chamber (this parameter was modified from 50 to 200 Torr in steps of 50 Torr). The ramping speed was of 40 °C/s for both vacuum and Ar/CdS post-deposition treatments. For thermal treatments under Ar/CdS atmosphere, CdS was introduced by positioning a 200 nm thick CdS-coated substrate to the surface of the CTO substrate, with CdS film in direct contact with CTO. The CdS film was grown by chemical bath deposition on glass substrates at 88 ± 1 °C of bath temperature, with a deposition time of 40 min. The methodology for synthesizing these CdS films follows the one described by Mathew, et al. [38], with the exception of molar proportions. In present work it was used cadmium acetate ($(CH_3COO)_2Cd{\cdot}2H_2O$, 1 mol), ammonium acetate ($C_2H_7NO_2$, 20 mol), ammonium hydroxide (NH_3, 0.85 mol), thiourea (CH_4N_2S, 3.45 mol), and water (58 mol). For each treatment, a new CdS film was used to guarantee that all the CTO films were in contact with the same amount of CdS. This method of annealing has been reported by T. Meng et al. [15].

2.2. Rapid thermal annealing system

RTA post-deposition of thin films was performed in a home-made system (Rapid Thermal System, RTA-001). The optical heating of the samples on both sides was achieved by two rows of 500 W Phillips halogen lamps (6 lamps per row.) The annealing process consisted of three phases, depicted in Fig. 1: ramp-up (10 s), a plateau period (corresponding to t_T) at fixed temperature (Ta in this work), and non-forced cooling. Samples were subjected to RTA in vacuum and Ar/CdS atmospheres at Ta=600 °C during t_T=5 s. The temperature ramp-up was set at 40 °C/s for all cases. Higher ramp rates caused lack of stability in treatment temperature, due to performance of the proportional-integral-differential, PID, controller (Novus 1200).

It is important to mention that previous to the thermal treatment