



## Rapid thermal annealing on ZnMgO window layer for improved performance of CdTe solar cells



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### ARTICLE INFO

#### Keywords:

ZnMgO  
Rapid thermal annealing  
CdTe solar cell

### ABSTRACT

Poor qualities of ZnMgO thin films are likely to be obtained at higher Mg content, which can decrease the performance of ZnMgO-based devices. This study focuses on improving the qualities of ZnMgO thin films to increase the performance of CdTe solar cell. It is found that the rapid thermal annealing (RTA) treatment increases the crystallinity, eliminates defects and improves the conductivity of ZnMgO thin films. These are helpful to suppress the recombination caused by bulk and interface defects as well as to reduce the cell's series resistance. The Fermi level moves close to conduction band and both the conduction and valence band energy shift lower relative to band energy of CdSSeTe film after RTA, which could not only increase the built-in voltage but also enhance the electron transport and block the hole recombination. As a result, the efficiency of CdTe solar cells is enhanced when using the RTA-treated ZnMgO, with maximum power conversion efficiency reaching values of 15.7%, which are much higher than those of the cells with the as-grown ZnMgO (11.6%). RTA is proved to be one of the excellent methods to control the properties of ZnMgO for improving the performance of CdTe solar cell.

### 1. Introduction

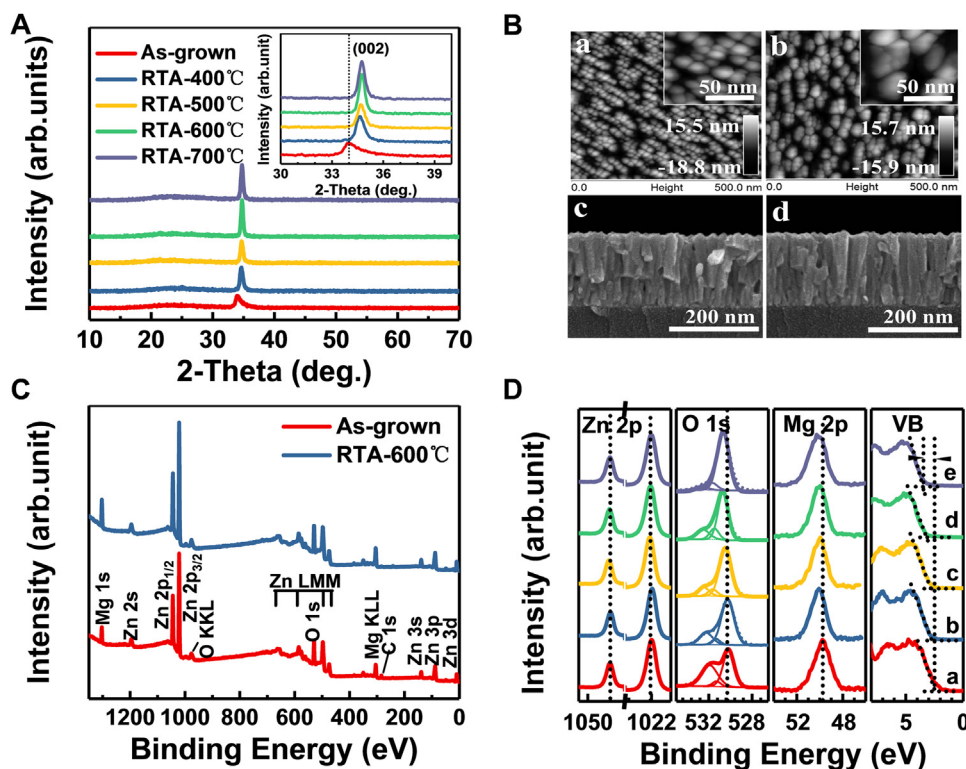
It has been reported that the chalcogenide photovoltaic devices with higher efficiency, such as CdTe, CIS, can be prepared with using the  $Zn_{1-x}Mg_xO$  (ZnMgO) as high resistance buffer layer or window layer [1–3]. This is not only because that the bandgap of ZnMgO can be increased by adjusting the magnesium content to improve the spectral response and to increase the short-circuit current density, but also because that the increase of magnesium content can result in the change of its electron affinity and contribute to the formation of appropriate heterojunction electric field distribution to inhibit the recombination of photo-generated carriers [4–6]. However, the big difference between the wurtzite structure of ZnO and rock salt structure of MgO will bring about the higher formation energy of ZnMgO. So there are much ZnO, MgO or ZnMgO phases that deviate from the required stoichiometric ratio. And the stability of ZnMgO thin films is in general poor in post process because of a lots of defects [7–11]. These limit the further increase of the photoelectric conversion efficiency of photovoltaic devices including ZnMgO window layer. And it is the reason that there are fewer publications to report the higher efficiency chalcogenide photovoltaic devices including ZnMgO window layer.

RF magnetron sputtering technology has been used to deposit ZnMgO thin films because of its advantages of easy control of composition and easy scaling of the process for the large area module. Although some researchers reported that the performance of ZnMgO thin films in RF magnetron technology could be optimized by adjusting substrate temperature, sputtering power, target materials, etc. [12–17], or by the treatment after deposition, such as oxygen plasma surface passivation, light soaking, etc. [18–20]. With the optimization of the process, the crystallinity of the ZnMgO thin film increases, and the defect decreases. However, above studies did not disclose the relation between ZnMgO characteristics and CdTe solar cell performance.

In this paper, the rapid thermal annealing (RTA) processes were developed for ZnMgO thin films which were deposited by RF magnetron sputtering in room temperature. The mechanism of ZnMgO thin films properties improvement were analyzed. The higher efficiency CdTe solar cells were prepared by using RTA-treated ZnMgO as windows layer.

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**Fig. 1.** Analysis of structure, morphology and electronic properties. (A) XRD patterns of ZnMgO thin films before and after RTA from 400 to 700 °C. The inset image is the corresponding magnified pattern of (002) peak. (B) AFM images and cross-sectional SEM images of ZnMgO thin films, (a, c) as-grown; (b, d) RTA at 600 °C. The Inset images in (a) and (b) show magnified details of sample surface obtained with AFM. (C) XPS survey spectra and (D) high-resolution XPS spectra for Zn 2p, Mg 2p, O 1s peaks and valence band (VB) spectra for ZnMgO thin films. The Auger O KLL, Zn LMM, Mg KLL and a weak of C 1s peaks were obtained in XPS survey spectra. (a) The as-grown and the RTA-treated ZnMgO thin films at (b) 400 °C (c) 500 °C (d) 600 °C (e) 700 °C.

## 2. Experimental details

### 2.1. ZnMgO thin film preparation and characterization

ZnMgO thin films were prepared on Corning Eagle XG glass substrate by RF sputtering using a ZnMgO target (Chengdu Ultra Pure Applied Materials, purity: 99.99%, MgO:ZnO = 20:80 mol%) at room temperature. The sputtering chamber was initially pumped down to  $5 \times 10^{-4}$  Pa, and then pure Ar gas was introduced through mass flow controllers to achieve the required pressure. During the sputtering, the deposition pressure was maintained at 1.5 Pa, and the power was kept at 100 W. The thickness of all films was controlled to be about 200 nm by adjusting the deposition time. After the deposition, the ZnMgO thin films were annealed at 1.0 Pa in Ar from 400 to 700 °C for 30 min using a RTA furnace (CHY-1100-RTP, Cheng Yi, China) and then were naturally cooled down to room temperature in the RTA furnace. The heating rate was kept at 10 °C/s.

The film thickness was determined by a step profilometer (XP-2, Ambios Technology Inc. USA). The structure was characterized by X-ray diffraction (XRD, Dandong Fangyuan Instrument Co. Ltd., China) in the 2-theta range of 10–70°. Surface morphology and the cross-sectional images of the ZnMgO thin films coated on the Eagle XG glass substrate were obtained from atomic force microscope (AFM, Bruker Nano Inc DI Multimode 8) and field emission scanning electron microscope (SEM, Hitachi S-4800), respectively. The compositions of the ZnMgO targets and films were analyzed by X-ray fluorescence spectrometer (XRF, Rigaku ZSX Primus II). The surface chemical analysis was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, ThermoFisher Scientific). Monochromatic Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) was used as excitation source. Prior to the XPS measurement, the films were cleaned by Ar<sup>+</sup> ions (500 eV) for 60 s to remove any potential surface contamination. All the obtained spectra were calibrated to the C1s peak at 284.8 eV and the core level peaks were analyzed using a nonlinear Shirley-type background. The Fermi level position ( $E_F$ ) was aligned to a binding energy ( $E_{bin} = E_F = 0$  eV) using clean Au metallic sample. The electrical properties were measured in van der Pauw

method through a Hall effect system with a set of a Keithley 7065 Hall effect card, 6485 picoammeter, 2182A nanovoltmeter, and 6220 constant current source. The contacts were made by soldering with high purity indium on the four corner of samples (size:  $10 \times 10$  mm<sup>2</sup>). The optical transmission spectra were measured using a UV–Vis–NIR grating spectrophotometer (Perkin-Elmer Lambda 950) in the wavelength range of 300–1000 nm and the transmitted intensity detected was normalized against the intensity detected without a sample in the optical path.

### 2.2. Solar cell fabrication and characterization

The device structures were Glass/FTO/ZnMgO/CdS/CdSe/CdTe/ZnTe:Cu/Au. The glass/FTO substrates (Pilkington Tec10) were washed with glass cleaner (Amway Corporation) firstly and rinsed with deionized water for several times. Then they were cleaned by ultrasonic bath in acetone and finally dried under air stream. The ZnMgO layers (~60 nm) were deposited by RF sputtering. The CdS (~35 nm) layers were grown by chemical bath deposition. The CdSe (~50 nm) layers were prepared by RF sputtering using a target supplied by Chengdu Ultra Pure Applied Materials. CdTe absorber layers (~4  $\mu$ m) were deposited by close spaced sublimation (purity 99.999%, KYD Material, China) at ~15 Torr in an Ar/O<sub>2</sub> mixed gas with oxygen volume content of 8%. The source evaporation temperature and the substrate temperature were 645 °C and 560 °C, respectively. Then the CdTe layers, covered by a thin layer of CdCl<sub>2</sub> using ultrasonic method, were annealed at 388 °C for 35 min in N<sub>2</sub> + O<sub>2</sub> (4:1) ambient. After heat treatment, the surface of CdTe films was etched using 0.2% bromine/methanol for 8 s. The ZnTe/ZnTe:Cu (35/70 nm, Cu 6% mol) bilayer back contacts were deposited by co-evaporation from ZnTe and Cu, followed by rapid thermal annealing process at 350 °C for 1.5 min in nitrogen ambient. All cells were complete by evaporation of Au contacts and defined by laser scribing into individual cells (cell area: 0.24 cm<sup>2</sup>).

The current–voltage characteristics were measured both under simulated AM1.5 sunlight at 100 mW cm<sup>-2</sup> irradiation (Keithley 2400-LV Source meter, ABET technologies Sun 3000 solar simulator) and in the

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