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Structural, optical and electrical properties of Nd-doped SnO_2 thin films fabricated by reactive magnetron sputtering for solar cell devices

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ABSTRACT

The use of photon conversion layers is an interesting way to improve the overall efficiency of solar cells. Herein we report on Nd-doped SnO_2 thin films with photon management property inserted further into CIGS based solar cells. The functionalized layers were deposited by reactive magnetron sputtering whose structural, optical and electrical properties were tuned by varying the deposition temperature. Careful analysis of the structure using XRD and XPS showed that the tetragonal rutile SnO_2 phase can be obtained at a deposition temperature as low as 100 °C. Transparency was found to be as high as 90% for all layers while the absorption edge is found to increase when increasing the deposition temperature up to 300 °C. The photoluminescence measurements under 325 nm UV laser excitation showed that 100 °C is needed for the optical activation of the rare earth. Despite the small amounts of Nd (around 0.62 at%), intense and narrow emission bands have been collected in the Near Infrared Region (NIR) which are characteristics of Nd^{3+} ions whose the ionic state was confirmed by the 3d XPS core levels. Thus, the emission spectra cover a good part of the spectrum useful to the solar cell. Photoluminescence excitation spectroscopy experiments were also carried out on Nd:SnO_2 samples to get insights on the energy transfer. By exciting in the deep UV from 250 to 400 nm intense Nd emission was collected giving an experimental evidence of the down-shifting process through a resonant energy transfer from the SnO_2 host matrix to the Nd^{3+} ions. Hall Effect measurements showed that the n-type character and good conductivity of the Nd doped SnO_2 films can be correlated to the highest optical activity of Nd in the matrix. An optimal condition is found for the Nd-doped SnO_2 film grown at 300 °C for which the highest PL and the best electrical data were measured. Finally, we show that the implementation of such optimized Nd–SnO_2 films on CIGS based solar cells serving as a transparent conducting oxide and a down shifting converter results in the best power conversion efficiency.

1. Introduction

Photon management by different means opens the opportunity to create new applications in diverse fields. In particular, the combination of rare earth (RE) elements with wide band gap semiconductors have stirred a lot of interest and recognized a lot of success in the technologies of lasers, optical fibers, fluorescent lamps, light emitting displays, bioscience and imaging [1,2]. In the field of solar energy, these combined materials can act as photon converter structures with functionalities such as down-shifting (DS), down-conversion (DC) or up-conversion (UC), which might enhance the solar cell efficiency [3–5]. The concept is that the incident photons from the solar spectrum can be converted to photons that match better the absorption wavelength range of the solar cell. For instance, by placing DC or DS layers in front of the solar cell, higher energy UV photons that cause thermalization losses can be converted into visible or near infrared lower energy photons, which can be absorbed by the cell [6–8]. Down conversion process is when more than one photon is produced from one high energy photon. Downshifting, on the other hand, is when one

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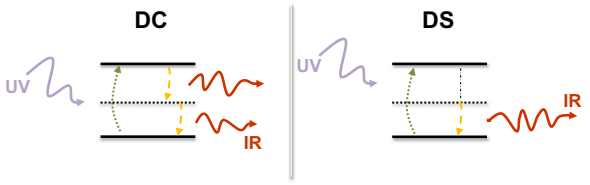

Fig. 1. Diagram illustrating down-conversion and down-shifting process.

high energy photon is converted to one lower energy photon (Fig. 1). Richards et al. have reported several interesting systems showing the role of lanthanides in DC and UC for Photovoltaic (PV) devices [9–11]. Since then, the researches on RE doped materials were significantly intensified.

For best knowledge of the authors, a lot of studies have been reported on RE doped ZnO thin films as photon converters, especially with Pr, Nd, Eu, Er and Yb [12–15] but only few on RE doped SnO_2 thin films. We focused our investigations on tin dioxide as a host material because it combines several advantages over other transparent-conducting oxides (TCO). This n-type semiconductor offers a wide band gap (about of 3.6 eV for the bulk material at room temperature) and high exciton binding energy (130 eV). It possesses a good conductivity and a high carrier concentration owing to the high concentration of native oxygen vacancies. Moreover, SnO_2 exhibits a high transparency in the visible range and a strong reflectivity in the NIR region [16]. In addition to the TCO properties, SnO_2 can be doped with trivalent rare earth elements (RE) such as Yb, Er, Eu, Ce, Sm and Nd [17–21], which generates novel properties without affecting transparency or other key properties thanks to the photoluminescence properties of these ions.

In this paper we present structural, optical and electrical properties of Nd doped SnO_2 thin films produced by reactive magnetron sputtering, a technique that allows a good control of the stoichiometry of the films and higher dopant insertion. We have monitored the photoluminescence properties of the Nd-doped SnO_2 films versus the deposition temperature. We show that for the films grown at temperatures up to 300 °C the incorporated Nd^{3+} ions are well inserted into the polycrystalline tetragonal SnO_2 structure and give rise to intense emission bands in the NIR region under UV laser excitation. We discuss the efficiency of the energy transfer from the SnO_2 host matrix to the Nd^{3+} ions. Finally, we demonstrate that the Nd:SnO_2 films can be used as down-shifter for CIGS based solar cells.

2. Experimental

Nd-doped SnO_2 thin films were deposited on p-type silicon Si (100) or quartz substrates using an Orion 3 Radio Frequency (RF) reactive magnetron sputtering from AJA International Co. the doping was performed by placing pure Nd metal disks on the top of pure Sn target. Argon and oxygen reactive gas were introduced in the sputtering chamber to synthesize Nd:SnO_x thin films. The optimized Ar/O_2 gas flow ratio was chosen at 2. The substrates were on top configuration with a substrate-to-target distance about 12 cm. The pressure and RF power were set at 3.4 mTorr and 50 W, respectively. To insure and improve the homogeneity of the layers, the substrate holder was rotating during the deposition process. Since the deposition temperature represents one of the important key parameters for dopant insertion and activation, the substrate temperature was varied from 15 up to 400 °C. The substrate holder was cooled with water cycles during the deposition.

The structural properties of the films were analyzed in the 20–80° 2θ range scan using Rigaku SmartLab X-ray diffractometer (XRD) with a $CuK\alpha_1$ incident beam of $\lambda = 0.154056$ nm and a monochromator at 45 kV and 200 mA. Prior each measurement, a systematic calibration on the Si (400) peak is performed. The films thicknesses were deduced from X-ray reflectometry (XRR) data. The Nd doping concentration of about 0.62 at% was measured using Rutherford Backscattering Spectroscopy (RBS). X-ray Photoelectron Spectroscopy (XPS) surface chemical analyses were carried out to investigate the chemical stoichiometry of SnO_x films as well as the Nd ionic state. The measurements were performed by mean of a Thermo Electron K-Alpha spectrometer using a monochromatic Al-Kα X-Ray source (1486.6 eV). The calibration was done using Cu and Au (Au $4f_{7/2}$ at 84.0 eV) samples following the ASTM-E-902-94 standard procedure. Acquisition parameters imposed in this study were the following: 400 µm spot size, 12 kV primary energy, 6.0 mA emission intensity, CAE 50 eV and 0.1 eV energy step size. Spectra were taken in several points to ensure the homogeneity of the surfaces, and no significant differences were observed. The transparency of the grown films was investigated in the 200–850 nm range using a (UV–vis-NIR) Perkin-Elmer Lambda 950 spectrophotometer. Finally, the photoluminescence measurements were performed in the UV–vis-NIR ranges using a He–Cd laser as an excitation source. The signals in the 350–950 nm range were recorded by means of cooled CCD camera, while the emission in between 800 and 1500 nm range was collected using an InP/InGaAs photomultiplier tube cooled at 190 K and a 600 grooves/nm grating equipped monochromator. Hall Effect measurements were employed to investigate the electrical properties of the Nd-doped SnO_2 films using an ECOPIA Hall Effect measurement system.

CdS/CIGS/Mo/glass structures were coated with Nd-doped SnO_2 films deposited at different temperatures and their current–voltage characteristics were measured under solar simulator (AM1.5 irradiation) to extract the photovoltaic parameters such as the open circuit voltage and the short circuit current.

3. Results and discussion

3.1. Structural properties

The Nd doped SnO_2 films were deposited at different temperatures ranging from 15 to 400 °C. Table 1 gives the films thickness of these films as deduced from the XRR method. Thanks to the control of deposition rate, the films were produced to have comparable thicknesses.

In the following the structural properties of these films will be discussed as well as the determination of phase composition and Nd ionic state.

Fig. 2 displays typical X-ray diffraction patterns of the Nd-doped SnO_2 thin films grown at different temperatures. As can be observed, the film deposited at 15 °C exhibits a broad diffraction band that covers a wide diffraction angles range (from 25° to 38°) which could suggest at first glance an amorphous structure. Furthermore, it is quite difficult to distinguish whether there are different SnO_x phases as numerous diffraction peaks of SnO and SnO_2 can be present in this range. To get a deep insight on this structure,

Table 1
Thickness, crystallites size and energy band gap values of the SnO_2:Nd layers deposited at different temperatures

Deposition temperature (°C)	Film thickness (nm)	Crystallites size (nm) (110)	(200)	Tauc gap (eV)
15	101.3	/	/	3.53 ± 0.05
100	102.1	7.1	51.5	3.35 ± 0.03
200	103.3	14.4	50.1	3.38 ± 0.03
300	92.54	21.1	48.5	3.15 ± 0.03
400	81.58	25.7	44	3.66 ± 0.05