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Improved efficiency of n-ZnO/p-Si based photovoltaic cells by band offset engineering

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ABSTRACT

The theoretical approach towards improving the photovoltaic response of n-ZnO/p-Si heterojunctions proposed by Knutsen et al. [Phys. Status Solidi A 210 (2013) 585–588] has been experimentally tested. AZO/n-$Zn_{(1-x)}Mg_xO$ layers were deposited at 160 °C on p-Si substrates by atomic layer deposition (ALD) with magnesium concentration in the 0–4 at% range. The examined devices showed a reduction of the conduction band offset from (0.63 ± 0.03) eV to (0.48 ± 0.03) eV. This decrease leads to a diminishing impact of recombination centers at the interface between zinc oxide based layers and silicon substrate, when the Mg content is below ~1.6 at%. In this range, the overall photovoltaic efficiency increased from ~3.7% to ~6.0%. As a next step, we tested solar cells with similar magnesium concentration in the $Zn_{(1-x)}Mg_xO$ layer, but deposited at 300 °C. Due to the higher deposition temperature, a further 1.1% increase in efficiency has been obtained. So far, this is the highest reported efficiency for a ZnO/Si heterojunction grown by ALD method, thus experimentally confirming the validity of the approaches here studied for raising the efficiency of heterojunctions solar cells based on n-ZnO/p-Si, while significantly reducing the fabrication complexity respect to conventional Si based devices as emphasized by Hussain et al. [Sol. Energy Mater. Sol. Cells 139 (2015) 95–100].

1. Introduction

Thin films based on highly doped ZnO have been mainly investigated as transparent conductive oxide (TCO) electrodes in various thin film PV technologies [1]. For instance, it is well established the use of an intrinsic ZnO and aluminum doped ZnO (AZO) bilayer on the CdS/$CuIn_{(1-x)}Ga_xSe_2$ (CIGS) heterostructure to achieve solar cells with approximately 20% efficiency [2,3]. In such devices the ZnO bilayer plays a minor role in establishing the heterojunction, unless, for example, the field zone extends throughout the whole CdS buffer [1]. In alternative structures, involving the direct deposition of the ZnO layer on the absorber, the band alignment plays a crucial role in the resulting efficiency as has been shown for the case of Cd free CIGS solar cells [4,5]. Similarly, recent numerical calculations indicate that a decrease in the conduction band offset (ΔE_C) appearing in n-ZnO/p-Si heterojunctions strongly reduces the impact of recombination centers at the interface between the two semiconducting materials [6]. This, in turn, enables high efficiency solar cells, while reducing the fabrication complexity respect to conventional Si based solar cells [7]. In this prospective, using $Zn_{(1-x)}Mg_xO$ represents a suitable way to tune ΔE_C since, it is well known that Mg incorporation is reducing the material electron affinity ($X_{Zn(1-x)MgxO}$), while enlarging the material bandgap ($E_{Zn(1-x)MgxO}$) [8]. This increase guarantees good transparency in the solar spectrum range [6–8]. However, so far this possibility has not been explored experimentally in detail. The aim of the present work is to study the effects of Mg incorporation (up to about 4 at%) on the conduction band offset of n-ZnO/p-Si heterojunctions and their photovoltaic (PV) performances. It is shown that by decreasing ΔE_C from ~0.63 eV to ~0.48 eV a corresponding rise in the solar cell efficiency from ~3.7% to ~6.0%, under standard test conditions (STC), is achieved and an additional ~1.1% increase in efficiency can be obtained by depositing the $Zn_{(1-x)}Mg_xO$ layer at 300 °C. In addition, the ZnO films in the present study were grown by ALD that is reasonably cheaper/simpler comparing to other deposition techniques like molecular beam epitaxy or metal organic chemical vapor deposition and appropriate for industrial applications in

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modern electronics, thus also promising in frames of today solar cell devices.

2. Experiment

In this work, we used silicon wafers (100) with a resistivity of 10 Ω cm and thickness of ~180 μm and glass as substrates. The Si and glass samples were cleaned in 2-propanol, acetone and deionized water for 5 min each in an ultrasonic cleaner and transferred into an ALD reactor Savannah 100 (Cambridge Nano-Tech). A first set of samples, where the $Zn_{(1-x)}Mg_xO$ layers were grown at 160 °C on the p-type silicon substrates with 4 different Mg content (labeled as samples A–D hereafter), were deposited by using diethylzinc, deionized water and bis(methylcyclopentadienyl) magnesium as a zinc, oxygen and magnesium precursor, respectively. The number of cycles was chosen to obtain films of comparable thickness (~350 nm). Subsequently, on top of selected samples, where the $Zn_{(1-x)}Mg_xO$ films were deposited on Si substrates, an aluminum doped zinc oxide (AZO) layer ~250 nm thick was grown at 160 °C using trimethylaluminum as Al precursor, while samples without the AZO layer were used for XRD characterization. The related ALD process conditions and doping procedure are described in detail elsewhere [9,10].

Finally, the Si wafer was subsequently cut into squares of $\sim 0.3 \times 0.3$ cm^2 size and Al ohmic contacts to the front AZO layer (~40 nm thick) and back silicon substrate (~150 nm thick) were deposited by an e-beam evaporation system (PVD 75, Kurt Lesker). The top contacts area was ~0.017 cm^2. The resulting PV structure is depicted in Fig. 1. The elemental analysis in the obtained layers deposited on Si was determined through Energy Dispersive X-ray Spectrometry (EDS) by using a Scanning Electron Microscope (SEM) Hitachi SU-70, at accelerating voltage of 5 kV. The thickness of the films deposited on Si and glass was measured both with a NanoCalc 2000® thin film reflectometer and a DektakXT® stylus profilometer after chemically etching steps. The X-ray diffraction (XRD) measurements were performed using a Philips X'Pert diffractometer with the Cu $K\alpha_1$ ($\lambda \sim 1.5406$ Å) monochromatic radiation in Θ–2Θ mode. Ohmic contact to the $Zn_{(1-x)}Mg_xO$ films deposited on glass were fabricated by e-beam evaporation of a Ti/Au bilayer (~20/~40 nm) with the PVD 75, Kurt Lesker, system or by soldering indium directly to the film surface. Subsequently, the electrical parameters of these $Zn_{(1-x)}Mg_xO$ films were extracted from RT Hall effect measurements performed in dark in the van der Pauw configuration using a permanent magnet, producing a magnetic field of about 0.4 T, provided by a RH2035 PhysTech system. The n-$Zn_{(1-x)}Mg_xO$/p-Si diodes were characterized by current–voltage (I–V) and capacitance–voltage (C–V) measurements carried out at room temperature (RT) using a Keithley 2601A and an Agilent E4980A current and capacitance meters, respectively. Ac-probing frequencies in the 1–250 kHz range were used in the latter case. The PV response was measured using an I–V curve tracer PET (Photo Emission Tech) for fast I–V measurements with a sun simulator of cl. AAA and illumination irradiance equal to 100 mW/cm^2. External quantum efficiency (EQE) was tested at 25 °C in the wavelength range of 300–1200 nm using a PVE300 system (Bentham. As shown in the next section, the highest PV response was obtained for the sample with a Mg content equal to ~1.6 at%. Hence a second set of samples (labelled as samples E hereafter) containing similar Mg content was grown at 300 °C to test the effect of the growth temperature on the device performances. Similar sample preparation procedures as well as same measurements conditions and instrumentations have been used in this case.

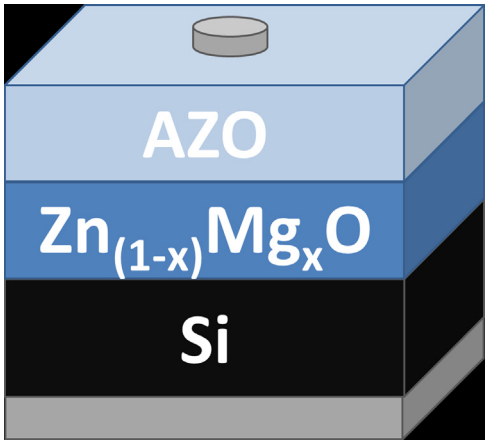

Fig. 1. Schematic draw of the studied solar cells structures (not scaled).

3. Results and discussion

3.1. Different magnesium concentration/content

3.1.1. $Zn_{(1-x)}Mg_xO$ layers electrical characteristics

The elemental composition measured by EDS of the $Zn_{(1-x)}Mg_xO$ films deposited on Si is summarized in Table 1, where the thickness of the layers determined by profilometry is also listed. The effect of Mg incorporation on the electrical properties of the $Zn_{(1-x)}Mg_xO$ layers grown on glass is shown in Fig. 2. It can be seen that the resistivity, $\rho_{Zn(1-x)MgxO}$, of the approximately 350 nm thick films slightly increases with increasing Mg content from about 10^{-2} Ω cm for sample A, up to about 6×10^{-2} Ω cm for sample D. Correspondingly, a factor of 2–3 decrease both in the mobility ($\mu_{Zn(1-x)MgxO}$) and carrier concentration ($n_{Zn(1-x)MgxO}$) is observed, if measurements performed on sample A and D are compared. The observed μ and n trends are consistent with the previously reported results, where difficulties in achieving high carrier concentrations and mobility values in $Zn_{(1-x)}Mg_xO$:Al have been attributed to a less efficient doping and effective mass increase, respectively, as a consequence of Mg introduction [11,12]. In addition, it is worth pointing out that the values of $n_{Zn(1-x)MgxO}$ and $\mu_{Zn(1-x)MgxO}$ measured for sample D are only about a factor 3 lower than the ones measured in case of the in-annealed $Zn_{(1-x)}Mg_xO$ films obtained by reactive magnetron sputtering with similar Mg content. Furthermore, lower $\rho_{Zn(1-x)MgxO}$ values are achievable by Al doping and this would be beneficial to the examined solar cell performance [11–13].

3.2. Device characteristics and band alignment versus Mg content

The dark I–V measurements carried out on selected heterostructures among the best performing for each Mg content, named for convenience also samples A, B, C and D, are shown in Fig. 3. The diodes exhibit rectification ratio of at least 3 orders of magnitude if the current values at ±3 V are compared. The investigations of the I–V characteristics have been performed over the whole

Table 1
Elemental concentration as derived from the EDS data and thickness of the films measured by profilometry.

	A	B	C	D
Zn [%]	53.3 ± 0.5	53.2 ± 0.4	52.2 ± 0.4	49.2 ± 0.4
Mg [%]	0	0.7 ± 0.2	1.6 ± 0.2	3.8 ± 0.4
O [%]	46.7 ± 0.5	46.1 ± 0.6	46.2 ± 0.6	47.0 ± 0.6
Thickness (nm)	355 ± 10	354 ± 6	380 ± 10	315 ± 10