Cr-doped ZnS for intermediate band solar cells

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ABSTRACT — **In this paper we present preliminary current-voltage characteristics of different ZnS/p-Si hetero-junction solar cells, under 1 sun illumination. The devices with Cr-doped ZnS show an increase in the short circuit current, and only a slight decrease in the open circuit voltage compared to the devices with undoped ZnS. The ZnS films were prepared using pulsed laser deposition on p-doped Si (100) substrates, and are highly (111) oriented. For the Cr-doped films absorption of sub-bandgap photons is observed in the UV-VIS wavelength range. The findings support the identification of Cr-doped ZnS as a promising intermediate band solar cell material.**

Index terms **— zinc compounds, chromium, thin films, photovoltaic cells**

I. INTRODUCTION

Intermediate band solar cells (IBSCs) are attracting increased attention due to their high efficiency limits.[1] In intermediate band (IB) materials an additional energy band is present inside the forbidden band gap, allowing low energy photons to be absorbed, and thus increasing the photo-generated current. If charge carriers are extracted from the conduction and valence band only, a high voltage over the cell can be maintained, resulting in the increased efficiency limit. Three types of IB materials have been attempted for the realization of IBSCs: i) InAs/GaAs and related quantum dot (QD) materials [2, 3] ii) dilute III–V nitrides (GaN_xAs_{1-x}) [4] and II–VI oxides (ZnO_xTe_{1-x}) [5] and iii) doping with a high density of transition metals (Ti-doped Si [6] and Cr-doped GaN [7]).

Most of these materials contain toxic or scarce elements, and thus non-toxic and abundant alternatives are needed and one candidate is Cr-doped ZnS. Simulations of the electronic properties of Cr-doped ZnS based on first principles, show that a partially filled intermediate band can form within the ZnS bandgap, due to the presence of the Cr atoms.[8] This intermediate band can then facilitate absorption of sub-bandgap photons, making Cr-doped ZnS a potential candidate for the realization of IBSCs.[8]

In this paper, we show preliminary results indicating an increased photo-generated current for a solar cell containing a Cr-doped ZnS layer, compared to a solar cell with an undoped ZnS layer.

II. EXPERIMENTAL DETAILS

The ZnS and Cr-doped ZnS films were grown on p-type Si (100) and quartz substrates using pulsed laser deposition (PLD) using a Lambda Physics COMPex Pro 110 laser charged with KrF (248 nm) operated at 5 Hz. The laser beam was focused onto a scanning target to create an energy density on the target surface of 4-5 J/cm^2. Polycrystalline, undoped ZnS and Cr-doped ZnS (nominally 6 at% Cr) targets were used. The background pressure of the PLD chamber before deposition was below 10^{-7} mbar. During deposition the chamber was back-filled with Ar, to a pressure of 3×10^{-3} mbar and 1×10^{-3} mbar for the undoped ZnS and Cr-doped ZnS films, respectively. The Si substrates were cleaned in acetone and isopropyl alcohol (IPA) in an ultrasonic bath, and etched in 5% HF for 3 minutes to remove the native oxide. The Si substrates were kept in IPA (for up to 20 minutes) until they were loaded into the vacuum chamber via a load-lock. Prior to deposition the Si substrates were heat treated in the vacuum chamber at 850˚C. The substrate temperature during deposition was 500˚C and 550˚C for the undoped and Cr-doped ZnS films, respectively.

The undoped and Cr-doped ZnS films were characterized by X-ray diffraction (XRD), Auger electron spectroscopy (AES), Scanning electron microscopy (SEM), and Atomic Force Microscopy (AFM). In addition the absorption coefficients were obtained from UV-VIS optical spectroscopy. The Cr concentration and the Zn/S ratio were measured by electron microprobe analysis (EMPA).

Simple ZnS/Si hetero-junction solar cells were made, consisting of an undoped or Cr-doped ZnS film on top of a p-type Si substrate. Two types of devices were made, with either point contacts or finger electrodes on the front. The devices with point contacts (1-2 mm in diameter, made of In) had InGa contacts on the back surfaces, while the devices with finger electrodes (Al/Au) had Al/Ti/Au back electrodes. All contacts were deposited at room temperature and were not annealed. The current-voltage characteristics of the devices, kept at 25˚C, were measured in dark, and under 1 sun illumination (AM1.5) using a calibrated solar simulator (ABET technologies Sun 2000).

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III. RESULTS AND DISCUSSION

A. Thin Film Characterization

Both the undoped and Cr-doped ZnS films were highly (111) oriented, as seen from the XRD diffractograms in Fig. 1. No Cr related XRD peaks were found, indicating that a separate Cr containing phase has not been formed. The FWHM of the (111) peak is 0.25˚ and 0.57˚ for undoped ZnS and Cr-doped ZnS, respectively, indicating a smaller grain size for the Cr-doped films, as can be seen form the SEM images in Fig. 2. The (111) peak positions of the Cr-doped and undoped ZnS films are 28.6˚ and 28.5˚, respectively. Correspondingly, the d spacing of ZnS (111) plane is increased from 3.116 Å to 3.131 Å when doping with Cr.

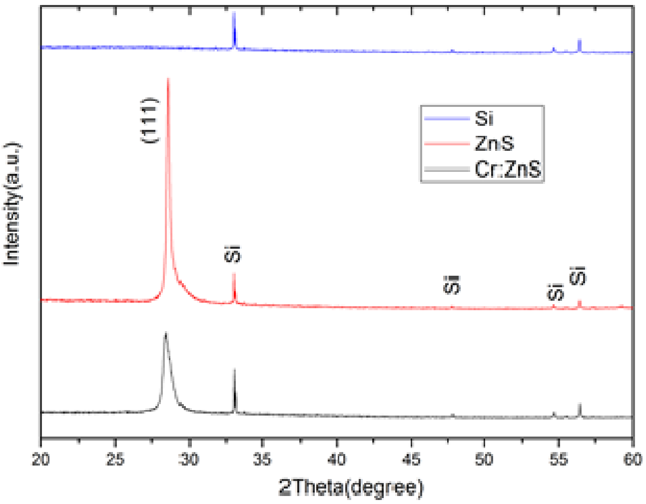

Fig. 1. XRD diffractograms of Cr-doped ZnS (bottom black curve), undoped ZnS (red) films, and the Si substrate (blue).

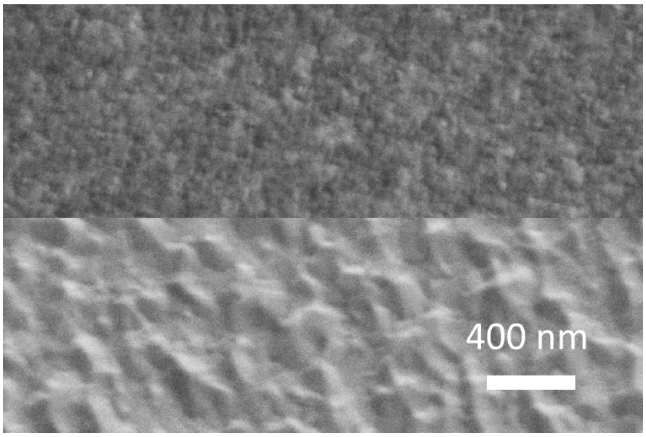

Fig. 2. SEM images of Cr-doped ZnS (top), undoped ZnS (bottom) films grown on p-type Si(100).

From the EMPA data (not shown) it was concluded that the Cr contents was approximately 3% in the Cr-doped ZnS films. AES mapping (not shown) indicated that the Cr-doping was uniform, as no Cr clusters were detected.

The absorption coefficients obtained from the optical spectroscopy of the ZnS films deposited on quartz are plotted in Fig. 3. We clearly see an increase of the absorption coefficient below the ZnS bandgap of 3.6 eV for the Cr-doped ZnS compared with undoped ZnS. There are two broad absorption peaks centered at around 2.0 eV and 2.9 eV, respectively. The two absorption peaks are related to Cr^{3+} at octahedrally coordinated sites, indicating that that the incorporated Cr ions enter the interstitial sites of ZnS lattice.[9] The Cr ions can also enter in Zn sites and will then result in absorption lines in the infrared.

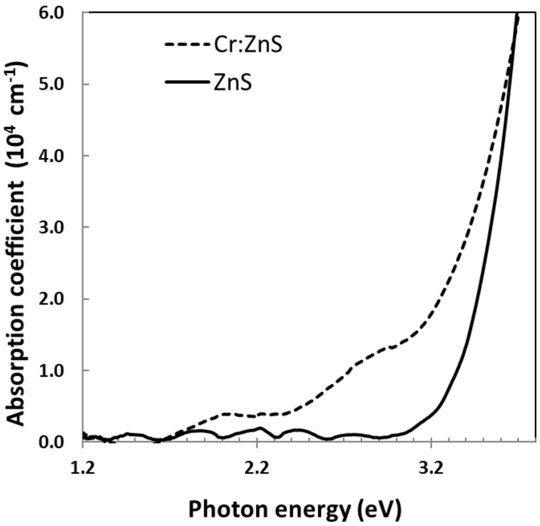

Fig. 3. Absorption coefficient of the Cr-doped ZnS (dashed curve) deposited by PLD at 300°C, and of undoped ZnS (solid line) deposited by MBE at room temperature, both on quartz substrates.

B. Device Characterization

The ZnS films were deposited in boron doped Si substrates, and contacts were applied so that the current-voltage characteristics could be obtained. In Fig. 4 the absolute value of the dark current is plotted as a function of the applied voltage for the devices with point contacts. Both ZnS/Si devices show rectifying behavior, and we thus conclude that the as-deposited undoped and Cr-doped ZnS films are n-type. We see from Fig. 4 that the reverse saturation current is larger in the device with Cr-doping, and relate this to a poorer crystalline quality.

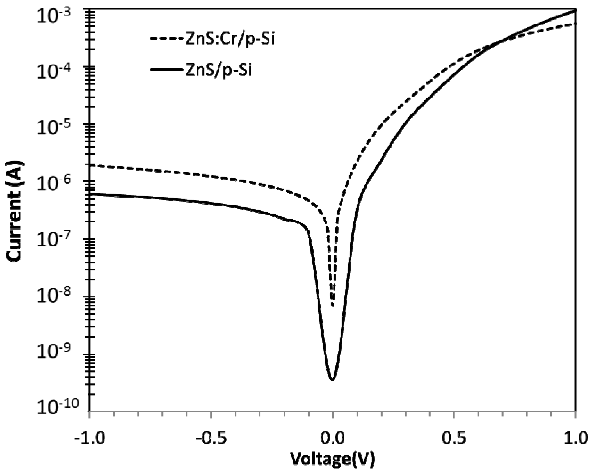

Fig. 4. Current—voltage characteristics in the dark of the heterojunction devices with point contacts: Cr-doped ZnS/Si (dashed curve) and undoped ZnS/Si (solid line) cells.

The current density as a function of applied voltage under 1 sun AM1.5 illumination for the (approximately 3 x 4 mm^2) devices with point contacts are shown in Fig. 5. We see that the overall performance is poor, but the short circuit current density, J_{sc}, is strongly enhanced in the Cr-doped device compared to the undoped. Please note that since the undoped and the Cr-doped ZnS films do not have the same thickness, the relative increase in J_{sc} due to the Cr-doping is difficult to quantify. The undoped ZnS has a thickness of 380 nm, while the Cr-doped is 150 nm thick.

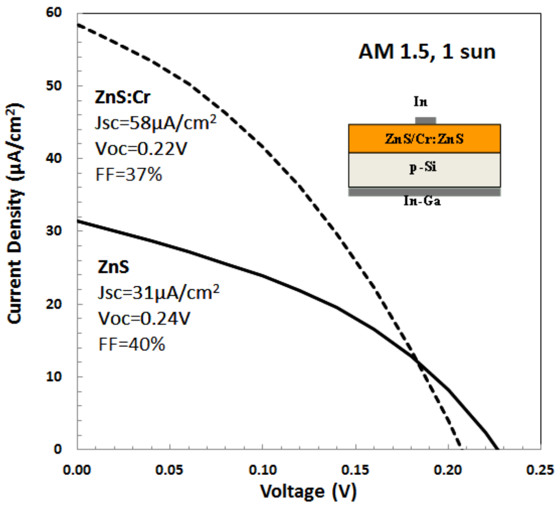

Fig. 5. Current-voltage characteristics of the ZnS/Si devices with point contacts under 1 sun AM1.5 illumination.

The increase in J_{sc} can qualitatively be explained as follows: In the undoped ZnS film, only a small fraction of the incoming light will be absorbed, and most of the light is absorbed in the underlying Si base. However, a lot of the current photo-generated in the base is not collected due to recombination in the ZnS film or its interfaces with the substrate or the contact. On the other hand, for the device with Cr-doping, photons with energy below the ZnS bandgap will be absorbed in the Cr-doped ZnS film. The current photo-generated in the ZnS film will more likely be collected, since it is generated closer to the contact, and this combined with increased absorption causes the increase in the J_{sc}.

The J_{sc} for the Cr-doped ZnS/Si device with point contact is somewhat larger than that for the Cr-doped GaN homo-junction cells reported in Ref. [7], while the open circuit voltage, V_{oc}, is lower. The reduced V_{oc} for our cells is mainly due to the low bandgap of the Si substrate, and is comparable to what has been reported for Bi_2S_3/Si hetero-junction cells.[10] In hetero-junction solar cells the V_{oc} is limited by the smallest bandgap.[11] There is probably a high density of non-radiative recombination centers in both the ZnS films that severely reduces the V_{oc} for both the undoped and Cr-doped devices. In addition the series resistance is likely quite high, as indicated by the low fill factor, FF.

From Fig. 5 we see that the V_{oc} for the device with Cr-doping is slightly lower than for the device without Cr-doping. This is attributed to the increased recombination via the Cr related energy levels in the bandgap. A reduced V_{oc} can also be a result of thermal/electronic coupling between the Cr states and the conduction or valence band, in either Si or ZnS, or with the electrode. If this coupling is not present the Cr states will have one (or more) separate quasi Fermi levels, and the device will have three quasi Fermi levels. One of the requirements for an intermediate band material will then be fulfilled. Based on the present data we can not determine whether there is coupling or not.

The low value for the short circuit current density is partly due to the lack of an anti-reflective coating, and is probably also due to short diffusion lengths and parasitic resistance. In addition, a potential barrier is formed in the conduction band at the ZnS/Si interface, and this impedes the carrier collection.

To increase the short circuit current density, Al/Au finger front electrodes were made by magnetron sputtering (Al) and e-beam (Au) using a shadow mask. The finger width is 0.5 mm and the spacing between the fingers is 1 mm, and the total cell area approximately 10 x 10 mm^2. Al/Ti/Au electrodes were deposited on the backside of the devices. For the two cells with finger front contacts we also made the undoped and Cr-doped films with more comparable thicknesses: 305 nm for the Cr-doped and 275 nm for the undoped ZnS film.

Current-voltage characteristics of the devices with finger front electrodes under 1 sun AM 1.5 are shown in Fig. 6. Again the device with the Cr-doped ZnS performs better than the one with undoped ZnS. We see a large increase in short circuit current density of the Cr-doped ZnS/Si device with finger electrode compared to the one with point contact, from 58 µA/cm^2 to 2.7 mA/cm^2. The open circuit voltage is also increased. For the undoped ZnS/Si device, the increase in J_{sc} is less than for the Cr-doped ZnS/Si device. Both devices with finger electrodes show a reduced fill factor compared to the point contact devices. This may be caused by a higher sensitivity, due to the larger contacted area, to pinholes and/or scratches in the films that might reduce the shunt resistance. Also the series resistance seems to be increased for the finger electrode devices.

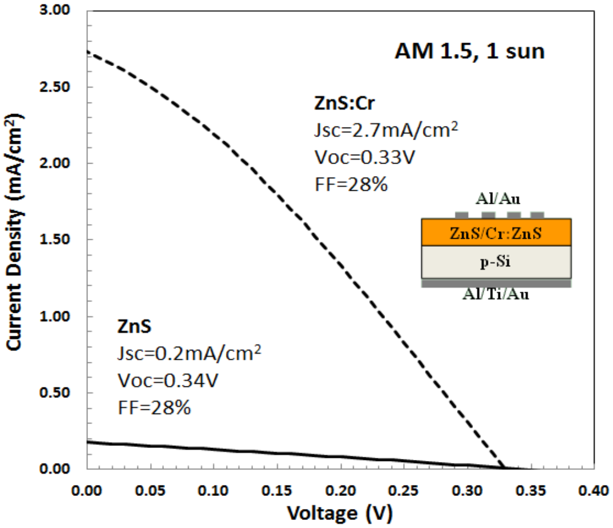

Fig. 6. Current-voltage characteristics of the ZnS/Si hetero-junction solar cells with finger electrodes under 1 sun AM1.5 illumination.

V. CONCLUSIONS

In this paper we have presented preliminary current-voltage characteristics of ZnS/p-Si hetero-junction solar cells, under 1 sun illumination. The ZnS films were either undoped or Cr-doped. The devices with Cr-doped ZnS show an increase in the short circuit current, and only a slight decrease in the open circuit voltage compared to the device with undoped ZnS. The ZnS films were prepared using pulsed laser deposition, and were highly (111) oriented. For the Cr-doped films absorption of sub ZnS bandgap photons is observed in the UV-VIS wavelength area. The results support the identification of Cr-doped ZnS as a promising intermediate band solar cell material, although further work is needed to improve the transport properties of the ZnS films and the contacts.

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