Low-cost 3D nanocomposite solar cells obtained by electrodeposition of CuInSe\textsubscript{2}

M. Valdés\textsuperscript{a,b}, M.A. Frontini\textsuperscript{a}, M. Vázquez\textsuperscript{a,*}, A. Goossens\textsuperscript{b}

\textsuperscript{a}División Corrosión, INTEMA, Facultad de Ingeniería, Universidad Nacional de Mar del Plata, J.B. Justo 4302, B7608FDQ Mar del Plata, Argentina

\textsuperscript{b}Optoelectronic Materials, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Available online 10 July 2007

Abstract

Thin CuInSe\textsubscript{2} films have been prepared by electrodeposition from a single bath aqueous solution on both dense and nanoporous TiO\textsubscript{2}. The films are deposited potentiostatically using a N\textsubscript{2}-purged electrolyte at different potentials. Various deposition times and solution compositions have been employed. The effect of annealing in air and in argon at different temperatures and times is also investigated. Thin films and nanocomposites of TiO\textsubscript{2} and CuInSe\textsubscript{2} have been studied with electron microscopy, X-ray diffraction, Raman spectroscopy, and optical absorption spectroscopy. After a thermal anneal in argon at 350 °C for 30 min excellent CuInSe\textsubscript{2} is obtained. In particular the nominal crystal structure and the bandgap of 1.0 eV are found. Although pinholes are present occasionally, good samples with diode curves showing a rectification ratio of 24 at ±1 V are obtained. Upon irradiation with simulated solar light of 1000 W m\textsuperscript{−2} a clear photoconductivity response is observed. Furthermore, also some photovoltaic energy conversion is found in TiO\textsubscript{2}/CuInSe\textsubscript{2} nanocomposites.

© 2007 Elsevier B.V. All rights reserved.

PACS : 73.40.Kp; 73.50.Pz

Keywords: TiO\textsubscript{2}; Nanoporous; CISE; Electrodeposition; Solar cells

1. Introduction

In order to reduce the production cost of solar cells, new cell concepts based on nanostructured materials have been developed. Grätzel and co-workers introduced an important advancement by using nanostructured titanium dioxide in dye-sensitized solar cells [1]. Others authors have used a similar concept to design new cells based on 3D inorganic heterojunctions, achieving conversion efficiencies of 5% using atomic layer deposition (ALD) and spray pyrolysis deposition (SPD) [2,3].

It is recognized that significant reduction of the production costs can be achieved if solar cells can be obtained under mild conditions and preferably without vacuum. Electrodeposition of chalcogenides has emerged as an alternative low-cost method for thin film solar cell production reaching remarkable conversion efficiencies [4–7]. Most authors have used metals or metallic coated glasses as substrate for electrodeposition.

In the present study, an inorganic heterojunction based in nanocomposite of TiO\textsubscript{2} (n-type semiconductor) and CuInSe\textsubscript{2} (p-type semiconductor) is pursued using electrodeposition. In a nanocomposite of TiO\textsubscript{2} and CuInSe\textsubscript{2} the pn junction is distributed in space, which allows reduction of the minority carrier diffusion length down to a few tens of nanometers. Exploring the variables associated to the electrodeposition process and thermal annealing to maximise the energy conversion efficiency of solar cells is the focal point of our current investigations.

2. Experimental

Glass coated with a transparent conducting oxide (TCO, Libbey Owens Ford, TEC 8/3 mm) is used as the substrate and is degreased in an ultrasonic bath with ethanol three times during 15 min.

Spray deposition is then applied to deposit a dense 150 nm thin film of anatase TiO\textsubscript{2} [8]. This film prevents direct contact
between CuInSe$_2$ and SnO$_2$:F (TCO), which short-circuits the cell. Next, a nanocrystalline anatase TiO$_2$ (nc-TiO$_2$) coating is applied using doctor blading [9]. These films consist of 9 nm or 25 nm crystallites sintered together at 450 °C for 6 h to form the electron-conducting matrix with a thickness of approximately 1 μm.

Electrodeposition of CuInSe$_2$ (CISe) is carried out at room temperature using aqueous solutions with different Cu:In:Se ratios in the electrolyte (1:1:1, 1:2:1, 1:2:2, 1:4:2). The composition of the aqueous solution used is 5 mM CuCl$_2$, 10 mM InCl$_3$ and 5 mM SeO$_2$ for the 1:2:1 electrolyte ratio and similar for the others. The pH of the bath is adjusted between 1.5 and 2.5 using diluted HCl solution. During the electrodeposition the solution is purged with nitrogen and bath temperature is maintained at room temperature. CISe thin films are deposited potentiostatically, using a three electrodes configuration. A standard calomel electrode (SCE) is used as reference and a Pt sheet of big area is the counter electrode. The substrates are square (2 cm × 2 cm) TiO$_2$ coated TCO glasses, as previously described. The electroactive geometrical area is confined by the cell design to 1.13 cm$^2$, but one should take into account that the internal surface area of nc-TiO$_2$ is much larger.

The electrodeposition process is controlled using a Princeton Applied Research Potentiostat/Galvanostat model 273. The films have been deposited at 4 different potentials varying between −0.7 and −1.0 V versus SCE during 60 min.

To improve the crystallinity of the as-deposited CISe films a post-deposition annealing is carried out at different temperatures between 300 and 450 °C in argon atmosphere.

The excess of Cu and Se is removed by etching the films in 0.5 M KCN aqueous solution for different periods of time (1–5 min) as is described in the literature [10].

The crystal structure of the samples is determined with X-ray diffraction (Bruker D8 Advanced Diffractometer) using Cu K$_\alpha$ radiation and Ni–Cu slits filter. The operation voltage and current used are 40 kV and 40 mA, respectively. The diffraction patterns are recorded from 2θ = 10° to 70°. Raman spectra are obtained using a Spectra Physics Millenia Nd:YVO$_4$ with a wavelength of 532 nm in the backscattering mode, a set of notch filters to remove the Raleigh scatterings and a 340 Spex monochromator equipped with an 1800 grooves/mm grating.

The optical properties of the films, i.e. absorption coefficient and the direct band gap energy $E_g$ are derived from the transmission spectra.

To investigate the photoresponse of the cells, current–voltage curves of representative devices such as SnO$_2$:F/TiO$_2$(100 nm)/CISe/graphite and SnO$_2$:F/TiO$_2$(100 nm)/nc-TiO$_2$/CISe/graphite are performed in the dark and under 1000 W m$^{-2}$ simulated solar irradiation (AM 1.5, K.H. Steuernagel Lichttechnik GmbH). In some samples evaporated gold dots (0.0314 cm$^2$) are used as back contacts.

3. Results and discussion

3.1. TiO$_2$ characterization

Fig. 1 presents XRD patterns of dense and nanostructured anatase TiO$_2$ thin films prepared by spray pyrolysis and doctor blade, respectively. In addition to the peaks related to the substrate (SnO$_2$:F), the main peaks of anatase TiO$_2$ (1 0 1) and (2 0 0) at 29.49° and 56.5°, respectively, are found in the diffractogram, indicating good crystallinity of the material. In the case of nc-TiO$_2$ of 25 nm an small peak of rutile at 32° is also present. Fig. 2 presents a Raman spectrum of nc-TiO$_2$. The particle size in this case is 25 nm (Degussa, P25). Intense Raman scattering saturates the detector.

3.2. CISe characterization

Fig. 3 shows the X-ray diffraction patterns of the CISe film deposited on dense TiO$_2$ films before and after annealing in argon at 350 °C for 30 min. Annealing significantly improves the crystallinity of the CISe films. In both patterns, the characteristic peaks of the chalcogenite structure (1 1 2), (2 0 4) and (2 0 0/1 1 6) are present but only after annealing the peaks become narrow and intense, indicating full crystallization of the CuInSe$_2$ with a preferred orientation in the

![Fig. 1. XRD patterns of TCO/dense TiO$_2$/nc–TiO$_2$. nc-TiO$_2$ average particle size is 25 nm (full line) and 9 nm (dash line).](image1)

![Fig. 2. Raman spectrum of nc-TiO$_2$ (25 nm) deposited by doctor blade on TCO substrate.](image2)
Absorption spectra are recorded for as-deposited and annealed samples prepared at various potentials and deposition times. These data can be converted into \((ahv)^2\) versus \((hv)\) plots, so as to determine the band gap values \((E_g)\) of the films. The calculated \(E_g\) values of as-deposited CISe or for samples annealed under various conditions vary between 0.9 and 1.0 eV and are shown in Fig. 4. \(E_g\) values of films produced at different potentials or for different deposition times were found to be always close to 1.0 eV, in agreement with the reported values for the electrodeposited CISe thin films [11].

Typical Raman spectra of as deposited CISe films on dense TiO\(_2\) at different deposition times are presented in Fig. 5. The intensity of Raman peaks strongly depends on the surface morphology and the phase composition of the CISe films.

All the spectra contain the A\(_1\) mode between 175 and 178 cm\(^{-1}\), generally observed in CuInSe\(_2\), and an additional peak at 258 cm\(^{-1}\) [12]. The latter peak is related to the presence of a Cu\(_x\)Se secondary phase. At short deposition times (5 and 15 min) Cu\(_x\)Se seems to be dominant with respect to the CISe phase in the film but at longer deposition times (45 and mainly 60 min) the fraction of Cu\(_x\)Se phase becomes smaller. From this observation we postulate that the electrodeposition of CISe is induced by an initial deposition of CuSe, which later transforms into CuInSe\(_2\).

A well-known method to remove the Cu\(_x\)Se phase is etching the film in KCN. Etching can be done before or after the annealing the CISe films. When as-deposited films are etched in KCN, partial detachment of the film occurs already after 1 min. On the other hand, when annealed CISe films are etched, detachment no longer occurs. Therefore, in this work, all etching experiments are performed on annealed CISe films.

Fig. 6 shows Raman spectra of an annealed CISe film before and after a KCN etch. The signal at 258 cm\(^{-1}\), related to a Cu\(_x\)Se phase, is almost completely eliminated by etching.

Fig. 7 shows a SEM micrograph of a CISe film deposited on dense TiO\(_2\)/nc-TiO\(_2\). CISe films annealed at 350 °C show bigger particles, in the micrometer range, as preferred in solar cells.
3.3. I–V characterization

Fig. 8 presents the dark I–V response of the TiO₂–gold Schottky barrier. This is a simple measurement that can be used to check if the quality of the dense and nanocrystalline TiO₂ is good enough to be used in a solar cell device. The low current density values can be related with the resistance and thickness of the TiO₂/nc–TiO₂ (bi)layer. Despite this, the I–V curve behaves like that of a diode, with a resulting rectification ratio of 24 at +1 and −1 V.

The first solar cell device obtained at the moment is shown in Fig. 9. It consisted of SnO₂:F/TiO₂(100 nm)/nc-TiO₂/CISe/graphite. nc-TiO₂ has been prepared using 9 nm particles and the CISe is electrodeposited from a single bath, at −0.8 V for 1 h. Annealed at 350 °C in Ar during 30 min is performed. No further etching is carried out. Despite the low values of the open circuit potential (Vₒc) and the short-circuit current density (J(sc)) this is an interesting result since it implies that it is possible to electrodeposit CISe inside the pores of nc-TiO₂. By optimizing the annealing and etching processes, the conversion efficiency is expected to improve significantly.

Fig. 9 shows a photoconductivity of a factor 2 at 1 V, while the photocurrent is 0.28 mA cm⁻². Fast electron–hole recombination destroys most of the photovoltaic activity. By applying a buffer layer we expect to accomplish significant reduction of the back reaction and hence an improvement of the energy conversion efficiency.

4. Conclusions

Anatase TiO₂ with a good semiconductor quality can be obtained by chemical spray pyrolysis deposition and doctor blading of nanoparticles, respectively. The integrity of the dense anatase TiO₂ film is very important to avoid pinholes. The thickness and resistance of this dense TiO₂ film is restricted to allow uniform and homogenous electrodeposition of CuInSe₂. A thickness of 150 nm of dense TiO₂ seems to be appropriate to obtain a good electrodeposited CISe film.

CuInSe₂ (CISe) has been obtained using one-step electrodeposition showing absorption, XRD and Raman spectra in good agreement with those reported for the crystalline material. When CISe is electrodeposited on top of a duplex layer composed of dense and nanocrystalline TiO₂ a heterojunction is formed.

Here we report the first 3D TiO₂/CuInSe₂ nanocomposite solar cell obtained by one-step electrodeposition of CISe. The low energy conversion in the illuminated I–V curve can be related with fast electron–hole recombination in the TiO₂/CISe interface. Current studies focus on introducing a buffer layer and on rapid thermal annealing in sulfur.

References