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The performance of sulphurized $TiO_2/In_2S_3/CuInSe_2$ solar cells.

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Abstract – An In_2S_3 buffer layer has been prepared by spray – pyrolysis on TiO_2/TCO glass substrates. On top of them $CuInSe_2$ films have been electrodeposited from a single bath solution. CISe films have been deposited potentiostatically using a deareated electrolyte at different potentials. Each layer has been studied by electron microscopy, electrochemical impedance and optical absorption spectroscopy. After a thermal annealing stage in a sulphur atmosphere at 550^{O}C for 10-30 minutes the crystallinity of the resulting chalcogenide is excellent. In particular the nominal crystal structure and the band gap of 1.4 eV are found and a clear photoconductivity response is obtained.

TiO_2 has been prepared by spray-pyrolysis, using TCO glass as substrate. The temperature of the hot plate is set between 350 – 375ºC, later increased to 450 ºC for 30 minutes to enhance the crystallinity.

In_2S_3 has been sprayed on top of this layer. The hot plate is set on 300 ºC and kept 30 minutes after the spray. The In/S ratio was fixed to 1.2/8.

$CuInSe_2$ (CISe) is then electrodeposited at room temperature from a single aqueous bath containing $CuCl_2$, $InCl_3$ and SeO_2. The deposition is potentiostatic, with the potential ranging from -0.8 to - 1.1 V vs, SCE. Homogenous, black films of CISe are thus obtained.

The complete device was annealed at 550 ºC varying the time between 10-30 minutes. 0.5 g of sulphur are placed in the annealing chamber and heated at 350 ºC (melting starts at around 200-250ºC). The samples are placed in a “cold zone” (100 ºC) of the tube and when the temperature reaches 550 ºC they are moved to the “annealing zone” and kept there for a fixed time. Then they are moved back to the cold zone of the tube. Nitrogen is flashed during all the annealing. This thermal treatment changes the $CuInSe_2$ structure to a $CuInS_{(2-x)}Se_x$ (CISSe). To evaluate the transformation from CISe to CISSe films have been deposited on Mo substrates and annealed in the same conditions as those of the films deposited on $TCO/TiO_2/In_2S_3$ substrates.

After the annealing treatment, the samples are etched in 0.5 mol/L KCN for several minutes to remove secondary phases (CuSe or Cu_2Se) that are detrimental for the devices. X-ray analysis shows a complete transformation of the $CuInSe_2$ to $CuInS_2$ composition as is indicated in the change in the (112) amorphous CISe peak to a high cristallinity (112) CIS structure. This is a key step which governs the final composition of the chalcogenide layer and determines the overall performance of the solar cell.

. Figure 1 presents XRD patterns of the as deposited CISe films on Mo/glass substrate and the transformation that occurs after annealing in sulphur at 550 ºC during 30 minutes. As can be seen, a complete transformation takes place. SEM micrographs of CIS films show an homogenous material with regular-size particles (Figure 2). A promising solar cell device is shown in Figure 3. A Xe lamp was used a light source. In spite of the low values of the open circuit potential (V_{oc}) and the short-circuit current density (J_{sc}) this is a starting-point result, from which we can continue working in improving the conversion efficiency.

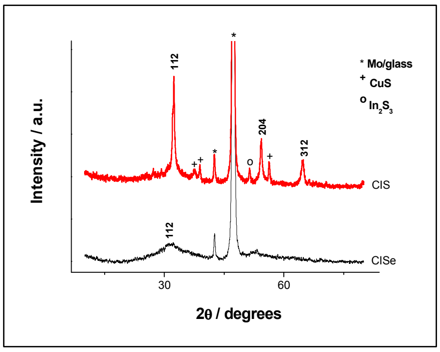

Figure 1: XRD patterns of CISe films deposited on Mo/glass substrates. (-) As deposited. (-) Annealed in sulphur at 550ºC during 30 min.

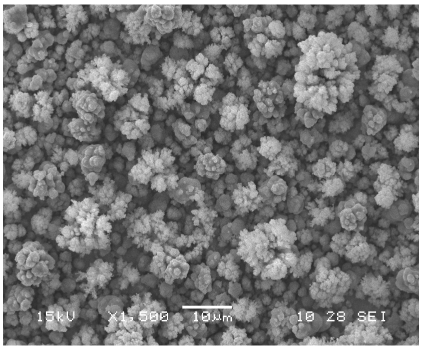

Figure 2: SEM image of annealed CISe precursor. The CISe film was deposited at -1 V vs. SCE during 1 hour, annealed at 550 ºC for 30 minutes in sulphur atmosphere.

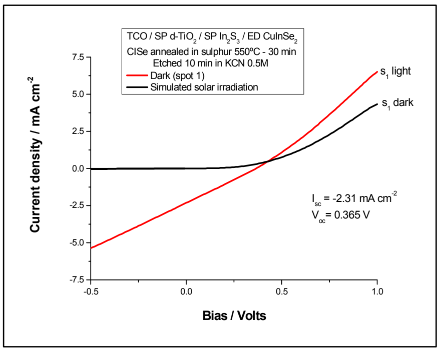

Figure 3: I-V curve (dark vs. illumination) performed on $TCO/TiO_2/In_2S_3/CuInSe_2$. The CISe film was deposited at -1.1 V vs. SCE during 1 hour, annealed in sulphur minutes.