

### 3D SOLID-STATE SOLAR CELLS BASED ON TiO<sub>2</sub>/CuInS<sub>2</sub> HETEROJUNCTIONS

MARIAN NANU, JOOP SCHOONMAN, AND ALBERT GOOSSENS

*Laboratory for Inorganic Chemistry, 43 Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands.*

The major drawback of the present generation of photovoltaic solar cells is their laborious, energy consuming, and costly production. Therefore, a completely new approach is desired. With the advent of dye-sensitized (Grätzel-type) solar cells, C60/polymer, and hybrid nanocrystal / polymer bulk heterojunctions, challenging alternatives are offered, although serious complications are still to be eliminated. A major concern in these alternatives is their poor stability if operating in full sunlight. The cells must be sealed rigorously to avoid reaction with oxygen and water. All-solid, completely inorganic, bulk heterojunctions do not require expensive sealing, but have been pursued with limited success so far. Here, we report a new approach towards what is referred to as the 3D-solar cell concept. In this type of nanocomposite, a wide bandgap n-type semiconducting oxide and a p-type visible light sensitive semiconductor are mixed on a nanometer scale. This solar cell concept may open a new horizon in the manufacture of future photovoltaic devices. We employed Atomic-Layer Chemical Vapour Deposition (AL-CVD) for infiltration of CuInS<sub>2</sub> inside the pores of nanostructured TiO<sub>2</sub>. First, a dense film of TiO<sub>2</sub> (~100 nm) is applied onto TCO-glass (SnO<sub>2</sub>:F). On top of this, a 2 μm thick nanoporous TiO<sub>2</sub> film is applied with primary particles between 10 and 50 nm in diameter. Next, these substrates are infiltrated with CuInS<sub>2</sub> using AL-CVD. The process conditions are: 2 mbar reactor pressure, temperature between 350 and 500 °C, and CuCl, InCl<sub>3</sub>, and H<sub>2</sub>S as precursors.

The chemical composition of the cells is investigated with X-ray diffraction, Raman spectroscopy, and photoluminescence spectroscopy. CuInS<sub>2</sub> films have the chalcopyrite crystal structure with a minor fraction of the Cu-Au ordered structure. The fraction of the Cu-Au phase can be determined with Raman spectroscopy and is about 5% in volume. Cu-Au is associated with the presence of anti-site point defects. Photoluminescence has been used to determine the energy levels associated to these anti-site defects, being 0.07 eV for  $In_{Cu}^{\bullet}$  and 0.15 eV for  $Cu_{In}^{\prime\prime}$ . The efficiency of CuInS<sub>2</sub> (CIS) solar cells is determined by the presence of anti-site defects because they introduce energy levels in the band gap, which determine the conductivity type and the minority carrier lifetime.

The electrical properties of nanostructured TiO<sub>2</sub>/CuInS<sub>2</sub> heterojunctions are investigated by studying Current-Voltage (IV) curves, Time of Flight (TOF), Impedance Spectroscopy (IS), and Deep-Level Transient Spectroscopy (DLTS) as a function of temperature. Preliminary results give us strong indications that these cells behave different in dark than dye-sensitized solar cells (Grätzel-type). The IV curves recorded in the dark shows space-charge limited current behaviours, with an activation energy for the hole mobility of 150 meV, which is associated to holes trapped on the anti-site defects  $Cu_{In}^{\prime\prime}$ . The energy levels of electron and hole traps derived with IV, IS and DLTS techniques agree with those found in our photoluminescence study. TOF results indicate that drift rather than diffusion governs the charge transport.

Since alignment of the conduction bands is required an In<sub>2</sub>S<sub>3</sub> buffer layer must be applied. The solar cells show photovoltaic activity between 360 and 900 nm with a maximum monochromatic incident photon-to current conversion efficiency of 80%. If AM1.5 irradiation is applied, the open-circuit voltage is 0.49 V, the short circuit current 18 mA cm<sup>-2</sup>, and the fill factor 0.44, which add up to an overall energy conversion efficiency of 4%. This is twice the performance of the best inorganic 3D solar cell reported so far.

**TOPICS + KEYWORDS:** 3D Solar Cells, Atomic-Layer Chemical Vapour Deposition, nanocomposite