All-solid semiconductor sensitized solar cells made by electrodeposition

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ETA-solar cells are presently based on ZnO nanowires or nanocrystalline TiO_2. The two n-type wide bandgap semiconductors (Eg ~ 3.3 eV) ZnO and TiO_2 are sensitized by an extremely thin layer of a semiconductor which absorbs in the visible (1 < Eg < 2 eV) such as CdSe, CdS, In_2S_3, $CuInS_2$ and Sb_2S_3 (1, 2). The majority of the ETA-solar cells are completed with CuSCN a p-type wide bandgap semiconductor (Eg ~ 3.4 eV). The ETA solar cells belong to the family of sensitized nanostructured solar cells, which include dye-sensitized and quantum-dots solar cells. The major advantage of the sensitized nanostructured solar cells stands in the low cost fabrication methods which are the following: doctor blade, electrochemical deposition, spray pyrolysis, SILAR or ILGAR, chemical bath deposition, solution casting etc. In order to facilitate the assembly of the solar cells and to reduce cost of production, it would be very attractive to fabricate the ETA-solar cells using one single technique of deposition such as the electrochemical one. For example ZnO/CdSe/CuSCN solar cells already use this technique to make the arrays of ZnO nanowires and the CdSe absorber layer (3). For the other components, the spray pyrolysis is used for the deposition of the ZnO electronic buffer layer directly on the conductive glass substrate, while solution casting allows impregnation of the ZnO/CdSe nanowire arrays with CuSCN. Optimization of all the fabrication steps, dimensions and thickness of the various components lead to ZnO/CdSe/CuSCN solar cells exhibiting record energy conversion efficiency of ~3.2 eV (4). This paper investigates the possibility to prepare the ZnO layer buffer and CuSCN layer by electrodeposition.

Electrodeposition of ZnO compact buffer layer

The ZnO nanowires were made using the O_2 reduction method. The same method allowed the formation of a compact ZnO layer providing the modification of some deposition parameters such as the $ZnCl_2$ precursor and KCl supporting electrolyte concentrations, the temperature. On such ZnO layers made galvanostatically or potentiostatically, ZnO nanowires with large diameter could be electrodeposited (5, 6).

Electrodeposition of CuSCN layer and CuSCN nanowires. CuSCN crystalline layers were electrodeposited in aqueous or organic electrolyte, with or without complexing agent, respectively (7-9). The deposition in organic solution, i.e. ethanol containing $Cu(BF_4)_2$ and KSCN allowed a good impregnation of the β-phase CuSCN within the array of ZnO nanowires when the temperature of the solution was maintained at 5 °C (10). In the aqueous solution containing $CuSO_4$, KSCN and TEA complexing agent, the electrodeposited CuSCN impregnated well the ZnO nanowire arrays. But, it did not recover homogeneously the top of the nanowires, the surface morphology being much rougher than that of the CuSCN obtained in the organic solution. The electrical properties of the glass/ZnO_{buffer}/$ZnO_{nanowire}$/CuSCN obtained structures were compared with those obtained with the CuSCN made by solution casting.

By modifying the composition of the aqueous solution, it was possible to obtain arrays of p-type CuSCN nanowires (11). Depending on the substrate morphology, nanowires with diameters between 50 and 380 nm with length up to 1.8 µm could be obtained (12). CuSCN nanowire growth was a very fast deposition process compared with that of ZnO and the CuSCN nanowires were obtained with lower current densities. CuSCN nanowires with the same length than ZnO nanowires, were obtained 6 times faster and the reached current densities were 10 times lower. Those results open the route to built inversed ETA-solar cells. In the inversed configuration, the CuSCN p-type nanowires are first grown on conductive substrate, then they are sensitized with an extremely thin absorber layer and it is the ZnO n-type wide band gap semiconductor that is impregnating the CuSCN/absorber nanowires. The fact that ZnO and CuSCN nanowires could be successfully grown on glass and plastic (polyethylene terephthalate (PET) covered with indium tin oxide (ITO)) and metallic (12) is very attractive for ETA-solar cell production. .

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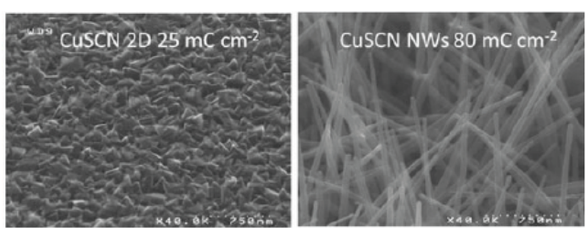

Figure 1. Electrochemical deposition of CuSCN. (left) compact layer deposited on a conductive glass substrate, (right) array of CuSCN nanowires deposited on the CuSCN compact layer.