

Sb₂S₃-based ETA solar cells

Yafit Itzhaik, Olivia Niitsoo, Miles Page and Gary Hodes

Dept. of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

The ETA (Extremely Thin Absorber) cell is an analogue of the solid state dye-sensitized cell, where the semiconductor absorber separates interpenetrating electron and hole conductors. The absorbing semiconductor is locally very thin (typically tens of nm) but because of the porous structure, the optical thickness is much greater. This means photogenerated electrons and holes travel a very short distance before being separated by injection into the electron and hole conductors. The electron conductor is usually TiO₂ or ZnO while the hole conductor can be a range of materials, of which CuSCN is one of the most common. The best ETA cell reported to date, based on an In₂S₃ absorber on ZnO with a CuSCN hole conductor, gave nearly 3.4% solar conversion efficiency [1].

In this report, we describe ETA cells using Sb₂S₃ as the light absorber with TiO₂ as the electron conductor and CuSCN as the hole conductor. Except for the Au contact deposition on the CuSCN, all the preparation steps are solution based. Starting from commercial FTO conducting glass, a dense TiO₂ film is deposited by spin coating from titanium isopropoxide solution and annealed, followed by a porous TiO₂ layer (P25), also by spin coating and annealing. A buffer layer of In-OH-S is deposited by chemical bath deposition (CBD) followed by Sb₂S₃ also by CBD. The amorphous Sb₂S₃ is annealed in N₂ at 300°C for 30 min to convert the as-deposited amorphous Sb₂S₃ (which showed little photoactivity) to crystalline stibnite. The annealed samples are removed from the hot furnace and allowed to cool in air (see below). After treatment with an aqueous KSCN solution, a solution of CuSCN in propyl sulphide was infiltrated into the porous film. Finally, a gold contact was deposited (sputtered or evaporated) onto the CuSCN.

There are several important steps which allowed us to reach the relatively high efficiencies (3.36% solar conversion efficiency; up to 80% peak external quantum efficiency and close to 100% internal peak quantum efficiency) we obtained.

One is the removal of the annealed Sb_2S_3 from the hot furnace to cool in air. This results in formation of an oxide layer on the Sb_2S_3 which apparently acts as a passivation layer. Samples allowed to cool in N_2 were not as good.

The In-OH-S 'buffer' layer, commonly used in such cells, may not be essential, although up to now, we have obtained our best cells using it (most of our experiments up to now used this buffer layer). Fairly good cells have been made with direct deposition of Sb_2S_3 onto the TiO_2 . It may be that the oxide passivation layer on the Sb_2S_3 is sufficient.

The KSCN treatment is also important: poor cell parameters are obtained if this step is skipped. It is possible that this treatment dopes the CuSCN and decreases the cell resistance (this decrease is seen in dark current-voltage measurements).

A very important parameter is aging of the cells: cells improve (current and fill factor) gradually with time after being assembled. This improvement may be completed within a few days but can often continue for weeks or even months. It is believed that this aging, which has been seen in CuSCN-based dye cells, is related to slow loss of residual propyl sulphide from the cell [2].

Finally, we carried out some preliminary operational stability tests on these cells. Continuous exposure to 60 mW/cm^2 equivalent solar radiation for 3 days under maximum power conditions led to no more than 10% decrease in power output, and most of this loss was regained when the cells were allowed to stand in the dark for some hours.

References

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2. O'Regan B.; Lenzmann F.; Muis R.; Wienke J. *Chem. Mater.* **2002**, *14*, 5023.