30 Years of Electrodeposition of Semi-conductors for Industrial Applications : Dreams, Realities and Dreams Again !

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In late 70's the work of Kroger on cadmium telluride electrodeposition has opened the modern adventure of the electrodeposition of semiconductors. Thanks to site selectivity provided by the free energy of formation of cadmium telluride, a unique process to control the composition close to the stoichiometric was evidenced and explained. Cadmium telluride layers with high structural quality in the as-deposited state and with semiconducting properties demonstrated that growing semiconductors from aqueous solutions in an unprecedented simple form was possible. This opened immense perspectives to use the electrodeposition approach for large scale and low cost processing of semiconductor devices, especially thin film solar cells. This was indeed the case when electrodeposited cadmium telluride modules at the square meter scale crossed the 10% efficiency level for thin film solar cells in 2000 after 15 years of intensive R&D efforts. Unfortunately the technology crushed down for non scientific reasons a few years later while the competing closed space vapor transport approach started its take off. Since that time the electrodeposition of CdTe has not recovered. However in the mean time, the electrodeposition of an even more complicated compound, CIGS $CuInGa(Se,S)_2$, has taken off. Basic studies started in the 1990's and we obtained a world record in 1994 using one step electrodeposition of CIS with a 6.4% efficiency. Further studies with sulfides led us to a new record of 11.3% in 2003, and allowed us to launch industrial developments which culminate today with the results of Nexcis on module fabrication. In parallel great success was obtained by Solopower in USA. In these insteances sequential electrodeposition is mainly used, as it appeared to be easier to implement at the industrial level. However we pursued our challenge to develop one step electrodeposition processes and recently we succeeded in developing a route based on mixed oxide/hydroxide deposition, reaching an efficiency of 12.4%. As in the initial Kroger's theory the free energy of formation of oxygen bonds allows the underpotential deposition of indium and gallium with remarkable control. This will give us the occasion to talk about the deposition of oxide semiconductors, which is experiencing a great success, as in the case of zinc oxide, which we have introduced in 1996. What will be the future of the electrodeposition of semiconductors? Beyond the ongoing direct competition with classical techniques for thin layer deposition, we think that there are dramatic opportunities to use the unique properties of electrodeposition for nanostructures as well as hybrid materials for new devices. In addition, selective deposition allows localized and template deposition. An example will be given in the field of solar cells based on microcells arrays which have been recently introduced in our laboratory