Electrodeposition of Semiconductors

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Electrodepostion (ED), which is widely used for metal or metallic alloys, for long time, appeared more later for semiconductors. We can associate the real birth of this field to the pioneering work by Kröger et al. in 1978 on cathodic deposition of CdTe. It is interesting to note that 24 years after CdTe is also the first material to open the age of large scale industrial applications for semiconductor electroplating, thanks to its “success story” for photovoltaics. This example is being followed by the synthesis of $Cu(In,Ga)Se_2$, a complex quaternary compound and may be followed by ZnO, a transparent conducting oxide, in the future.

Despite this success and all the progress done, many fundamental aspects of the ED of semiconductors are still not known precisely, in particular the deposition mechanism itself. The understanding and control of extrinsic doping, the role of the semiconducting properties of the electrode during the deposition (current transport mechanisms through the film, charge transfer at the interface, role of back contacts, photoinduced effects…) are other examples. Growth and shape control by additives are still at the prehistoric age as compared to metals… These are open areas of investigation

Concerning the electrodeposition mechanism, one of the most important specificity of the electrodeposition of compound semiconductors brings us back to Kröger’s work, when he explained the self regulated composition observed in CdTe films as a consequence of the high free energy of formation of this compound. Most of the recent works on either chalcogenides (sulfides, selenides, tellurides), oxides or other emerging compounds like thiocyanates, halides confirm the importance and the accuracy of this concept. It extends the UPD theory from monolayer deposition to bulk growth. Strong UPD effects allows site recognition processes during the growth, favoring the atomic arrangements in the deposits. This has been illustrated recently by the development of the Electrochemical Atomic Layer Epitaxy (ECALE) technique, which uses directly successive UPD steps in different solutions to form II-VI or III-V compounds. One step Epitaxial electrodeposition of semiconductor layers, dots, nanopillars, for chalcogenides, oxides is another example of optimal use of generalized Kröger’s concepts. In some cases (like for ZnO), the electrodeposition mechanism can even be considered as an electrochemically induced surface precipitation.

These considerations on mechanistic aspects show that the electrodeposition of semiconductors is now able to escape from its initial task of being only a cheap material provider technique. In this classical approach, mainly studied up to now, ED was used for the deposition of films, often thermally annealed, and introduced in classical solid state semiconductor structures. We can consider that this approach do not to take full benefit of the possibilities given by growth processes from solutions, at low temperature, under unique electrochemical assistance. This is clearly changing at the moment and more and more research works aim to obtain new structures, new functionalities, directly from the electodepoition step. One can highlight the growth of nanostructured semiconductors (oxides, chalcogenides) in foreign matrixes (organic or inorgatic templates), in the form of dots or wires, the formation of nanoporous semiconductor films by playing with the addition of poisoning species in the solution. Deposition of hybrid structures between semiconductors and organic molecules is also exemplified by results on the deposition of single cristalline nanoporous ZnO resulting from the interaction and incorporation of dye molecules during ED.

These new devices mainly follow “ready to use” approaches after the ED step. This should stimulate fundamental studies on the deposition mechanisms under such new complex conditions, and the development of inovative applications bringing electrodeposition of semiconductors at the entrance door of nanotechnologies and self organization bottom up strategies.