Electrodeposition of nanocrystalline and nanostructured semiconductors

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In common with other relatively low-temperature solution synthesis techniques, electrodeposition of semiconductors typically results in a small crystal size. This is clearly advantageous when the goal is formation of nanocrystalline materials. There are many different ways of electrodepositing semiconductors and different tactics to control crystal size and nanostructure of the resulting films. An overview of work carried out in this field will be presented here. The present discussion will be limited to non-template deposition. In addition, electrochemical dissolution to prepare nanostructures (e.g., porous Si) will not be discussed here.

Deposition of Cd chalcogenides from dissolved chalcogen in organic solvents – most commonly DMSO – has long been known to give films with crystal size down to 4 nm or even less. Major factors which affect crystal size are nature of the anions of the metal salts and surface-active agents in the electrolyte[1,2], pulse plating[2] and, where epitaxial deposition occurs, the lattice mismatch between the substrate and semiconductor[3]. Recently, the shape of electrodeposited epitaxial CdSe nanocrystals has been varied, from more or less symmetric (hemi)spheres to rounded columns or square pyramids by varying the deposition current density and temperature[4]. Not only crystal size and shape, but also crystal phase can be controlled by the nature of the substrate and high pressure rocksalt CdSe nanocrystals have been electrodeposited in a metastable state[5,6].

Semiconductor nanocrystals have been formed by first depositing metal nanoparticles from a solution of metal ions, followed by electrochemical oxidation of the nanoparticles to oxide (the oxide itself is often a semiconductor) and then displacement of the oxygen by another anion, such as sulphide or iodide. The conversion from metal to metal oxide to metal salt occurs on a particle-by-particle basis; that is, each metal nanoparticle is converted into a semiconductor nanoparticle. The final nanocrystals deposited on graphite are usually epitaxial with a narrow size distribution and a strong photoluminescence tunable by the particle size[7,8].

Multilayers (including superlattices) of semiconductors can be deposited by exploiting mass transport control of one constituent (e.g., the more readily reduced metal) and employing pulse deposition to regularly modulate the composition (e.g., Pb-Tl-O)[9] and metal chalcogenides[10]. Not only the thicknesses of the two layers but also their compositions can be controlled in this manner. In one case, spontaneous potential oscillations which occurred during galvanostatic deposition of $Cu(Cu_2O)$ resulted in alternating layers of Cu_2O ($\leq$ 1.5 nm thick) and a Cu/Cu_2O nanocomposite (typically ca. 15 nm thick)[11]. Superlattices of a single compound, Tl_2O_3, have been deposited with alternating layers posssessing differing defect chemistries, determined by the potential used for each layer (high overpotential = oxygen vacancies; low overpotential = cation interstitials)[12].

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