

John Stickney

Department of Chemistry
University of Georgia
Athens, GA 30602
Phone: 706.542.1967
Fax: 706.542.9454
stickney@chem.uga.edu



:: ECALE abstract ::

Research

Our group is interested in the study and growth of thin film materials. We are developing the electrochemical form of atomic layer epitaxy (ALE) or atomic layer deposition (ALD). ALE is a method where atomic layers of the elements making up a compound are deposited in a cycle, using surface limited reactions. In that way, growth is always layer by layer, promoting the epitaxial growth high quality thin films. Electrochemical surface limited reactions are generally referred to as underpotential deposition, or UPD. UPD is the phenomenon where an element is deposited at a potential prior to (under) that needed to deposit the element on itself. Deposition is facilitated by the free energy of formation of a surface compound. That is, a solution containing a precursor for a first element is reacted at a controlled potential with a previously deposited atomic layer of a second element, until the surface is covered, forming a compound monolayer. In electrochemical ALE (EC-ALE), the solution is then exchanged for one containing a precursor to the second element, and from which an atomic layer of it is deposited at a controlled potential, completing the deposition of one monolayer of the compound. Thin films are grown by repeating this cycle as many times as desired.

Semiconductors investigated so far include II-VIs, IV-VIs and III-Vs. Currently, the majority of our work has involved growth of the II-VI compounds CdTe, CdSe, CdS, ZnTe, ZnSe, ZnS, HgSe and HgTe. Some work investigating growth of the III-V compounds GaAs, InSb, GaSb and InAs has been pursued, as has deposition of the turnery compound CuInSe₂. Recently, excellent cycles for the growth of PbSe and PbTe have been developed.

There are hundreds of studies reported in the literature concerning the electrochemical growth of compound semiconductors. There is even a commercial process for the formation of CdTe for photovoltaics. Most of these studies use a simpler, quicker method, referred to here as co-deposition, where a single solution containing precursors for both of them, is used to deposit both elements simultaneously at a controlled potential or current density. In terms of speed and simplicity, EC-ALE is not competitive with codeposition, however, the degrees of freedom available in co-deposition are severely limited compared to EC-ALE. EC-ALE provides much increased control over deposit structure, morphology, and composition, by having separately optimized solutions and potentials for each element. In addition, as EC-ALE is based on layer by layer growth, so that epitaxy can be facilitated and atomic layer control over deposit thickness is a by product.

Most of the materials we are depositing are compound semiconductors, and in general are optoelectronic materials. These compounds are used to form emitters and detectors: light emitting diodes, lasers,

photovoltaics, and photon sensors. They are characterized by their band gap, which determines the energies of photons emitted or detected by devices made with these materials.

The advantages of atomic layer control are evident in the formation of nanostructured materials. Quantum confinement is when the electronic states of a material are a function of the dimensions of the material. That is, when an optoelectronic material absorbs a photon, it creates an exciton, an electron hole pair. The nominal distance between the electron and hole is a function of the compound, and has been referred to as the Bohr radius. If the dimensions of the material are smaller than say the Bohr radius, the exciton is perturbed by the walls of the material in which it is confined. Just like a particle in a box, the separation between states increases the smaller the box. This frequently results in a blue shift in the band gap, a shift to higher energy of the photons emitted or absorbed by the material. The result is that if you can control the dimensions of the material in the nanometer range, you can manipulate the band gap, i.e. band gap engineering.

One way to achieve this is to make a superlattice, a material where very thin films of two materials are alternated. Frequently such films require individual films which are a few monolayers thick, and that is where atomic level control over the deposition process becomes useful. Using EC-ALE it is a simple process to form four monolayers of one compound and then four of a second, and then repeat this whole process in order to form a superlattice.

Superlattices are materials confined in only one dimension. By forming nanowires or nanoclusters, where there are two or three dimensions of confinement, much stronger confinement can be produced. Electrochemical formation of wires or clusters, becomes relatively easy with a template. That is, one of the nice things about electrodeposition is that it only takes place on an electrode, a conductive substrate, selective area deposition. By using a nanostructured electrode, nanostructured deposits are formed. Presently, both superlattices and nanoclusters have been formed using EC-ALE. Spectroscopy of these materials is carried out by Professor Uwe Happek in the Physics Department here at UGA.

Studies of EC-ALE are presently directed towards the growth of more and new materials, as well as superlattices and nanocrystals. In addition, as EC-ALE is a process based on surface limited electrochemical reactions, a significant effort is directed towards the surface chemistry central to the formation of these compounds.

Studies of film growth involve development of an automated electrochemical flow cell reactors, in which electrochemical ALE can be performed. Resulting deposits are characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), electron probe micro analysis (EPMA), ellipsometry, and inductively coupled plasma mass spectrometry (ICP-MS). In addition, as noted above, the optical properties of these materials are being studied in Physics here at UGA, using surface reflection FTIR, and photoconductivity. Photoelectrochemical studies are also underway in the Stickney lab.

In atomic level studies, a number of surface sensitive techniques are used to investigate the atomic layer formation. For many of these techniques, ultra high vacuum (UHV) is required. UHV surface analysis chambers used for these studies contain optics for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), thermal desorption spectroscopy (TDS), and scanning tunneling microscopy (STM). In addition, electrochemical cells have been directly interfaced to these chambers, so that substrates can be characterized before experiments, and deposits can be characterized after, all without exposure to air. In addition, STM is being performed in-situ, during deposition, to better understand the origins of particular defect structures. Recently, an electrochemical flow cell with a quartz crystal microbalance (QCM) has been used to follow both the currents for deposition and the mass changes as each atomic layer is deposited.

Publications

T.E. Lister, and J.L. Stickney, "CdSe Deposition on Au(111) by Electrochemical ALE," *Appl. Surface Sci.*, 103 (1996) 153.

M.P. Soriaga, and J.L. Stickney, "Vacuum Surface Techniques in Electroanalytical Chemistry," *Chem. Anal.*, N.Y., 139 (1996) 1.

T.E. Lister, and J.L. Stickney, "Atomic Level Studies of Se Electrodeposition on Au(111) and Au(110)," *J. Phys. Chem.*, 100, (1996) 19568.

Thomas A. Sorenson, D. Wayne Suggs, Iris Nandhakumar, and John L. Stickney "Phase Transitions in the Electrodeposition of Tellurium Atomic Layers on Au(100)", *J. Electroanal. Chem.*, 467 (1999) 270-281.

J. L. Stickney, " Electrochemical Atomic Layer epitaxy (EC-ALE): Nanoscale control in the electrodeposition of compound semiconductors", in *Advances in Electrochemical Science and Engineering*, Volume 7, editors: R. Alkire and D. Kolb, Wiley-VCH, (2001), p. 1.

T. L. Wade, R. Vaidyanathan, U. Happek, and J.L. Stickney, "Electrochemical Formation of a III-V Compound Semiconductor Superlattice: InAs/InSb", *J. Electroanal. Chem.*, 500 (2001) 322.

T. A. Sorenson, K. Varazo, D. W. Suggs, and J. L. Stickney, "Formation of and Phase Transitions in Electrodeposited Tellurium Atomic Layers on Au(111)", *Surface Science*, 470 (3) (2001) 197.

K. Varazo, M.D. Lay, T. A. Sorenson, and J.L. Stickney* Formation of the First Monolayers of CdTe on Au(111) by Electrochemical Atomic Layer Epitaxy (EC-ALE): Studied by LEED, Auger, XPS, and In-situ STM", *J. Electroanal. Chem.*, 522 (2002) 104.

M.D. Lay, K. Varazo, J. L. Stickney, "Structures of Cd atomic layers electrodeposited from chloride electrolytes, studies by LEED, Auger, XPS and STM," *J. Amer. Chem. Soc.*, 125 (2003) 1352.