Electrochemical Atomic Layer Deposition

by John L. Stickney

Electrodeposition has served as a thin film preparation method since the 19th century, though it is thought by some to be more prone to contamination and less precise than corresponding vacuum processes. With the introduction of the Cu Damascene process for the formation of interconnects in ultra large scale integration (ULSI), it has become clear however that electrodeposition can be as clean as any other thin film deposition technique. This article argues that electrochemical atomic layer deposition (E-ALD) can control deposition down to the single atomic layer, and may someday rival molecular beam epitaxy (MBE) for control in nanofilm growth. This Chalkboard tutorial discusses the principles on which E-ALD is based and the technological opportunities it provides.

Atomic layer deposition (ALD)[1] is a methodology for forming nanofilms of materials one atomic layer at a time using surface limited reactions (SLR). SLRs occur only at the substrate or deposit surface: once the surface (the limiting reagent) is covered the reaction stops. E-ALD is ALD in an electrochemical environment. Various names have been used for E-ALD, including electrochemical atomic layer epitaxy (EC-ALE),[2] EC-ALD, ECALE, and ECALD. Underpotential deposition (UPD)[3] is a type of electrochemical SLR, where an atomic layer of a first element is deposited on a second, at a potential prior to (under) that needed to deposit the first element on itself. The term "atomic layer" refers to a coverage less than a monolayer (ML), a ML being a unit of coverage particular to the deposit being formed. From a surface chemistry point of view, a ML is formed when there is one deposit atom for each surface atom. UPD is a thermodynamic phenomenon, where the interaction energy between the two elements is larger than the interaction of an element with itself, thus resulting in the formation of a surface compound or alloy.

In electrodeposition, metal ion reduction to the element,

$$M^{2+} + 2e^- = M \qquad (1)$$

is generally controlled by the applied potential, which dictates the activity ratio of products to reactants according to the Nernst equation:

$$E = E^0_{M^{2+}} - \frac{RT}{2F} ln \frac{Products}{Reactants} \qquad (2)$$

Conventionally, the product is a bulk metal with an activity of 1. In UPD, however, the product is an atomic layer, which has a different electronic structure than the bulk M, due to its interaction with the substrate. The activity of the product is then less than 1, shifting the equilibrium potential, and accounting for UPD. UPD occurs when the depositing element is more stable on the substrate than on itself. UPD is fundamentally an SLR, as long as the applied potential is under the formal potential (E°') for bulk deposition, in the given solution. Bulk deposits do not form at an underpotential, regardless of the deposition time.

Each pair of elements has its own UPD chemistry, which must be investigated to devise an E-ALD cycle. An E-ALD cycle is the sequence of steps used to deposit one stoichiometric layer of the desired material: this would be an atomic layer for a pure element, or a bi-layer of a 1:1 compound. The CdS E-ALD cycle (Fig. 1) is an illustrative example: an atomic layer of S is deposited on one of Cd, and one of Cd is deposited on one of S.

$$S^{2-} = S_{UPD} + 2e^-$$

$$Cd^{2+} + 2e^- = Cd_{UPD} \qquad (2)$$
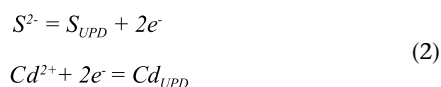
The cycle is composed of four steps: oxidative UPD of sulfur from a S^{2-} ion solution, a blank rinse, reductive UPD of cadmium from a Cd^{2+} ion solution, and a second blank rinse. Separate solutions are used for each reactant and different potentials for each cycle step. The use of separate solutions and potentials provides extensive control over deposit growth, composition, and morphology. A cycle is repeated to form a nanofilm, with the deposit thickness being a linear function of the number of cycles. This linear growth is a good indication of a layer by layer mechanism, and an ALD process.

There are a number of cycle chemistries that can be applied, depending on the depositing elements. The CdS cycle is an oxidative-reductive UPD cycle (O-R). In practice, few compounds can be formed using O-R, because of a lack of suitable negative oxidation state precursors (like S^{2-}), for which oxidative UPD is practicable. Other cycle chemistries include: reductive-reductive UPD (R-R), R-R with a reductive strip (R-R-R), R-R with an oxidative strip (R-R-O), bait and switch (B&S), and surface limited redox replacement (SLRR).

To achieve compound formation, the applied potentials and solution compositions for the E-ALD cycle should be optimized, resulting in a stoichiometric ratio of atomic layer coverages each cycle. As long as deposits are formed at underpotentials, the inherent stability associated with the formation of a stoichiometric compound will control the atomic layer coverages. For a binary compound like CdS, the atomic layer coverages will be identical, after the first few cycles. The amounts of an element deposited during each cycle will be a function of the potential chosen. The farther the UPD potential is from E°' (i.e., the larger the underpotential), the less of that element that will deposit. In turn, less of the second element will deposit, since its deposition is limited by the availability of the first element on the surface. Stoichiometric CdS will still result, but the growth will be at a lower rate (nm/cycle).

The above discussion suggests that each cycle results in a conformal compound layer, deposited over the whole surface. The rules for thin film formation still apply, however. Lattice matching with the substrate, for instance, is still an issue, and strain will increase as the number of cycles increases. Strain will be released when the critical thickness is achieved, with the formation of threading dislocations and other defects. The substrate may be a single crystal, wafer, polycrystalline
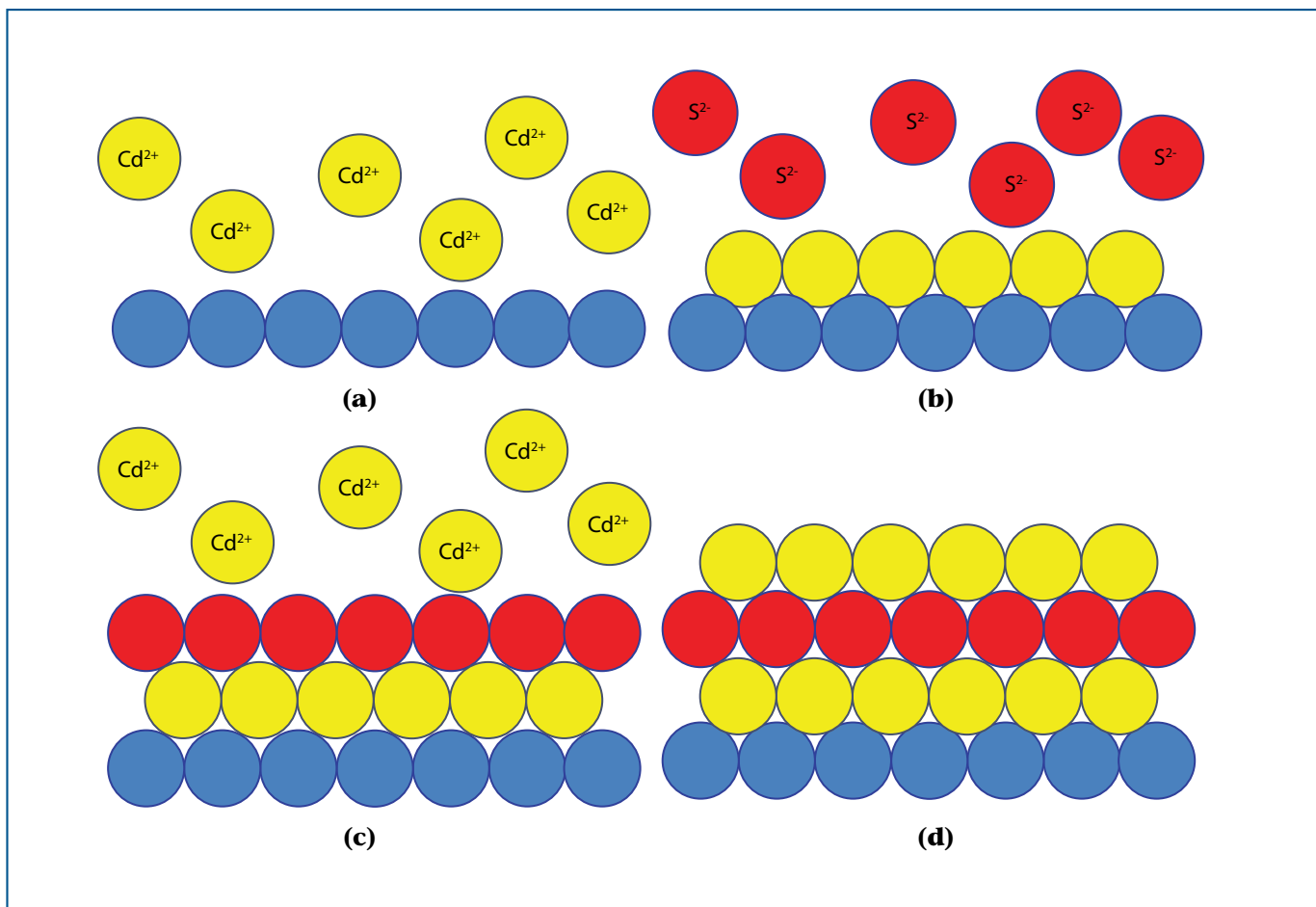
Fig. 1. *Scheme for a CdS E-ALD cycle. (a) exchange for Cd^{2+} ions, (b) Cd reductive UPD and exchange for S^{2-} ions, (c) S oxidative UPD and exchange for Cd^{2+} again, (d) one and a half bi-layers of CdS.*

film, foil, or powder. Each crystallographic facet will have a different affinity for the depositing element, and will result in a different coverage and interface structure. When various facets coalesce, grain boundaries will form, and the cycle conditions chosen will determine the resulting deposit morphology. Use of more aggressive conditions (smaller underpotentials) could cause roughening at grain boundaries, while use of larger underpotentials could minimize deposition at the boundaries (Fig. 2). Even when a single crystal is used as a substrate, there will be steps and defects, which may nucleate different deposit structures and orientations. The first E-ALD cycle is performed on the substrate, generally a different material. The optimal deposition conditions for the first few cycles may thus differ from the steady state conditions used to grow the remaining nanofilm, where the compound deposits on itself.

One of the major differences between E-ALD and the various vacuum and gas based deposition methodologies, besides use of a condensed phase, is temperature. E-ALD is performed at room temperature or under the boiling point of the solvent, all of which are considered "low temperature" for thin film formation. Despite formation at "low temperature," E-ALD forms deposits under equilibrium conditions. The deposition potential is applied until the current goes to zero and the composition and structure are constant, indicating that equilibrium has been reached for that potential. This is made possible by the exchange current (i_{ex}). Electrochemical deposition is a dynamic process, where atoms are depositing and dissolving at the same time. The measured current (i) is the difference between the deposition and dissolution flux, and when it is zero, equilibrium has been established. i_{ex} is a measure of the rate at which atoms are depositing and dissolving, at equilibrium. Ideally, atoms in high energy sites are dissolving and redepositing in more stable sites. The result is similar to thermal annealing, or to surface diffusion, in gas

or vacuum phase thin film deposition methods. Several other electrodeposition methodologies benefit from deposition at potentials near equilibrium; however, many involve overpotential deposition, where the contribution of i_{ex} is insignificant, so that deposited atoms tend not to redissolve, and deposits become disordered.

An increasing number of groups around the world have been using E-ALD to form materials. Nanofilms formed include: most of the II-VI compounds, including ZnSe [4], CdTe[2], and CdS[5], III-V compounds like InAs[6], IR detector materials InSb[7] and HgCdTe[8], thermoelectric materials such as the IV-VI compounds PbS[9], PbSe[10], and PbTe[10b, 11], as well as Sb_2Te_3[12] and Bi_2Te_3[12-13], and the photovoltaic materials CdTe[14], Ge, CIS, and CIGS. More recently, elemental deposits of metals have been formed using a cycle referred to as surface limited redox replacement (SLRR).[15] Metals deposited using an SLRR include: Pt[15-16], Ag, Cu[17], Pd, and Ru[17].

Most E-ALD deposits are formed using some type of electrochemical flow cell that allows for the rapid exchange of solutions, in combination with automation (Electrochemical ALD L.C., Athens, GA), the cycle can be programmed, and allowed to run for as many cycles as desired. Graduate students manually performing cycles usually tire and make mistakes somewhere after the 10th cycle. The more elements involved in the deposit, the more solution lines are required. More complex sequences of potentials and solution exchanges can be performed as well, such as the formation of a superlattice,[7,10b,18] where two or more materials are alternated to form materials with unique lattice constants, and optical and electronic properties (Fig. 2).
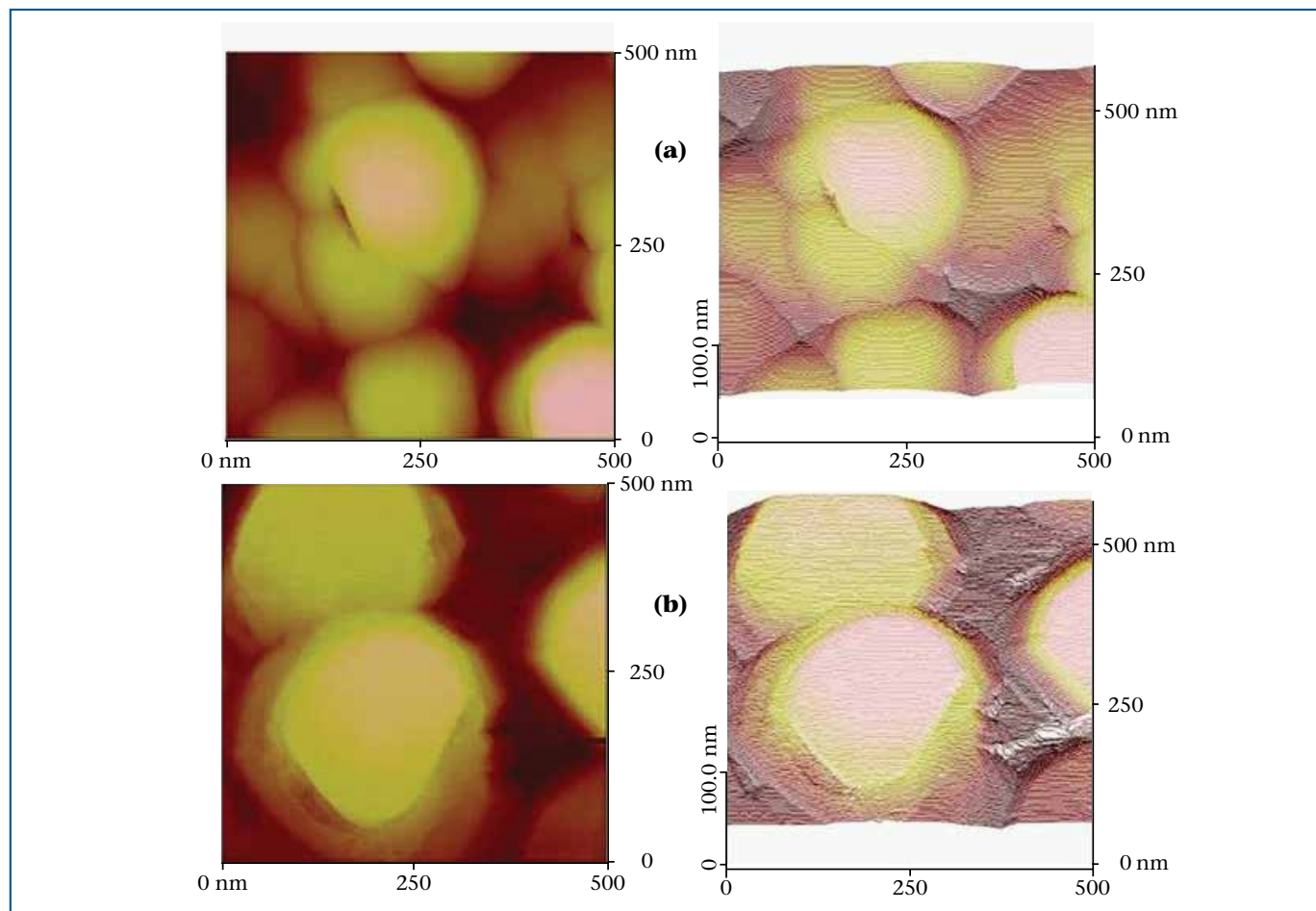
Fig. 2. *STM images: (a) Au vapor deposited on glass; (b) 30 superlattice periods, each consisting of 3 cycles of PbSe, followed by 15 cycles of PbTe, on Au vapor deposited on glass. Note the nearly atomically flat terraces resulting from the E-ALD deposit.*

About the Author

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