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Low Temperature Electrochemical Deposition of Highly Active Elements

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Abstract

Electrochemical methods are attractive for thin film deposition due to their simplicity, conformal and high rate deposition, the ability to easily make multilayers of different composition, ease of scale-up to large surface areas, and applicability to wide variety of different shapes and surface geometries. However, many elements from periodic table of commercial importance are too active to be electrodeposited from aqueous solution. Recent advances are briefly reviewed for room temperature methods for electrochemical deposition, including electrodeposition from ionic liquids, electrodeposition from organic solvents, combined electrodeposition and precipitation on liquid metal cathodes, and galvanic deposition. Recent studies of electrodeposition from ionic liquids include deposition of thick (40 µm) Al coatings on high-strength steel screws in a manufacturing environment; deposition of continuous Si, Ta and Nb coatings; and numerous interesting mechanistic studies. Recent studies of electrodeposition from organic solvents include Al coatings from the $AlCl_3$-dimethylsulfone electrolyte, which demonstrate that additives can be employed to suppress impurity incorporation and to improve the deposit quality, and thick (5-7 µm) and continuous Si coatings from $SiCl_4$ in acetonitrile. Galvanic deposition of Ti, Mo and Si coatings onto Al alloys has recently been reported, which is potentially much simpler and less expensive than electrodeposition from ionic liquids and organic solvents, but has complications associated with substrate consumption and coating adhesion.

Keywords

Electrodeposition, Electroless deposition, galvanic deposition, ionic liquids, organic electrolytes

1. Introduction

Electrochemical methods are attractive for thin film deposition due to their simplicity, conformal and high rate deposition, the ability to easily make multilayers of different composition, ease of scale-up to large surface areas, and applicability to wide variety of different shapes and surface geometries [1,2]. Due to its simplicity and flexibility, electrochemical methods are in general significantly less expensive than other methods for thin film deposition. Thin films deposited by electrochemical methods have a wide range of applications, including electrical contacts and interconnects, corrosion and wear resistance, decorative coatings, thin film photovoltaic devices, diffusion barriers, and a host of other applications.

The advantages of cost and simplicity for electrochemical thin film deposition depend to some extent on the use of aqueous electrolytes. While methods such as the Hall-Heroult process have been commercialized for electrodeposition of Al and other active elements from high temperature fluoride- and chloride-containing molten salt electrolytes, these processes have severe shortcomings that include high energy costs, difficult materials selection issues due to the possible corrosion, and toxic emission of fluoride and chloride compounds. For these reasons, development of low-temperature processes for electrochemical thin film deposition is highly desirable.

Figure 1 illustrates the range of elements for which aqueous electrodeposition is possible [3]. Although a fairly wide range of elements can be electrodeposited from aqueous electrolytes, in practice a smaller number have been commercially introduced [4]. The focus of this report is the recent literature on low temperature methods for electrochemical thin film deposition, including both aqueous and non-aqueous electrolytes, of active elements not easily electrodeposited from aqueous solution. The goal is to expand the library of elements for which commercial processes are available for electrochemical thin film deposition. In order to provide greater focus, the current discussion is limited predominantly to electrochemical deposition of Al, which is a prototype element for many non-aqueous plating processes; Si and Ge, which are the most common elemental semiconductors; and the refractory metals for which aqueous electrodeposition is not considered practical, including Ti, Zr, Hf, V, Nb, Ta, Mo, and W. The positions of Al, semiconductors Si and Ge, and the refractory metals are all indicated on Figure 1.

The term refractory metals generally refers to metallic elements that are unusually resistant to heat and wear, with high melting points and low vapor pressures. However, no rigorous definition exists for which specific elements this includes. The Refractory Metals Committee, organized by the Metallurgical Society of the American Institute of Mining, Metallurgical and Petroleum Engineers, uses the term “refractory” to include only metals with melting points above 1,900°C (3,500°F) [5]. On the other hand, the Metals Handbook published by the American Society for Metals, defines them as "metals having melting points above the range of Fe, Co and Ni [6]." The former definition includes only Nb, Ta, Mo, W and Re, while the latter also includes Ti, Cr, V, Zr, Hf, Ru, Os and Ir. Standard reduction potentials in aqueous acidic solutions are given in Table 1 for the elements considered in detail here [7]. Table 1 only provides a general reference point, since these values do not apply in organic solvents and room temperature ionic liquids, and multiple valance states and chelating agents may exist for each element.

Table 1: Reduction Potentials of Highly Active Elements in Aqueous Acid Electrolytes [7]

Electrochemical Reduction	E^0 (V vs. NHE)
$H_2MoO_4 + 6H^+ + 6e^- \rightarrow Mo + 4H_2O$	+0.11
$2H^+ + 2e^- \rightarrow H_2$	**0.00**
$GeO_2 + 4H^+ + 4e^- \rightarrow Ge + 2H_2O$	-0.01
$MoO_2 + 4H^+ + 4e^- \rightarrow Mo + 2H_2O$	-0.15
$TaF_7^{2-} + 5e^- \rightarrow Ta + 7F^-$	-0.45
$Nb_2O_5 + 10H^+ + 10e^- \rightarrow 2Nb + 5H_2O$	-0.65
$Ta_2O_5 + 10H^+ + 10e^- \rightarrow 2Ta + 5H_2O$	-0.81
$SiO_2 + 4H^+ + 4e^- \rightarrow Si + 2H_2O$	-0.89
$Nb^{3+} + 3e^- \rightarrow Nb$	-1.1
$TiF_6^{2-} + 4e^- \rightarrow Ti + 6F^-$	-1.19
$SiF_6^{2-} + 4e^- \rightarrow Si + 6F^-$	-1.2
$Ti^{2+} + 2e^- \rightarrow Ti$	-1.63
$Al^{3+} + 3e^- \rightarrow Al$	-1.67
$AlF_6^{3-} + 3e^- \rightarrow Al + 6F^-$	-2.07

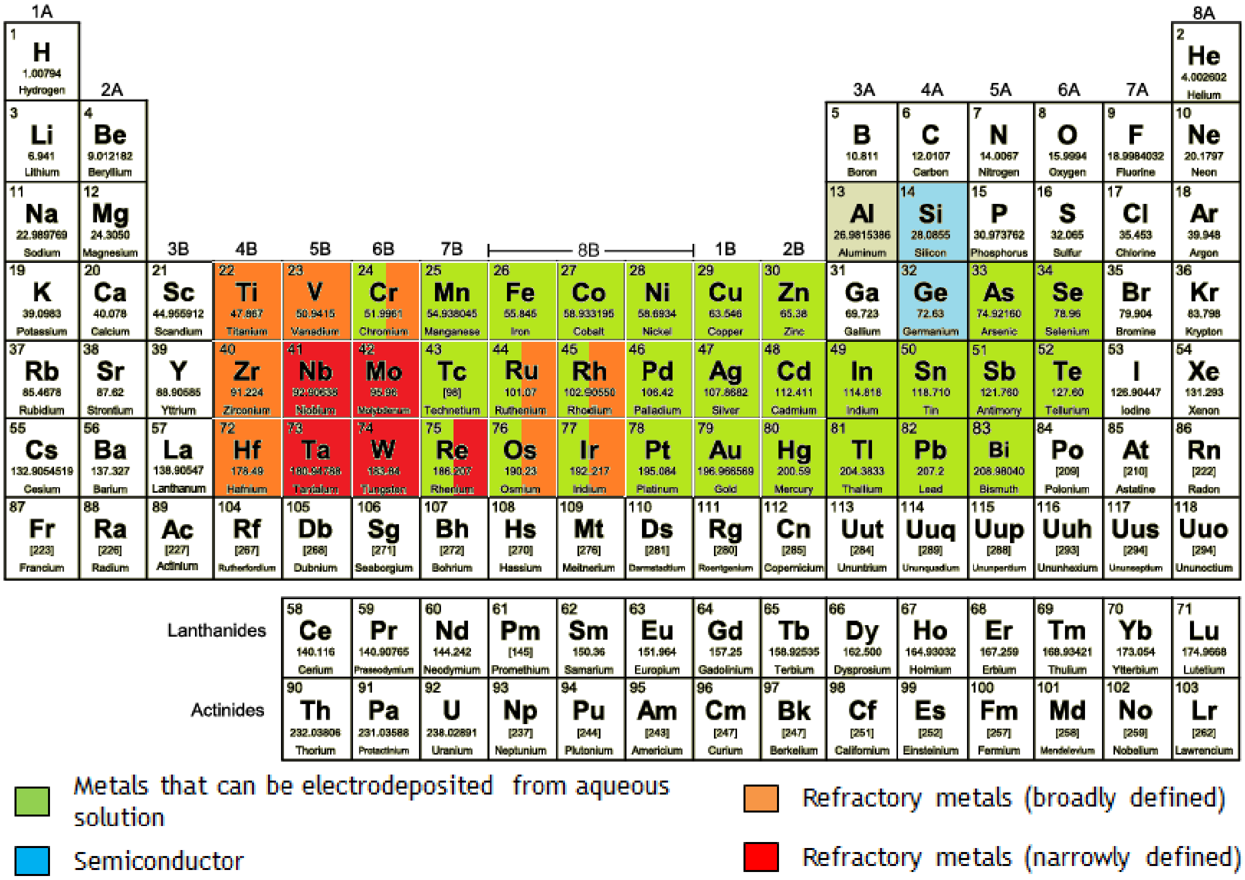
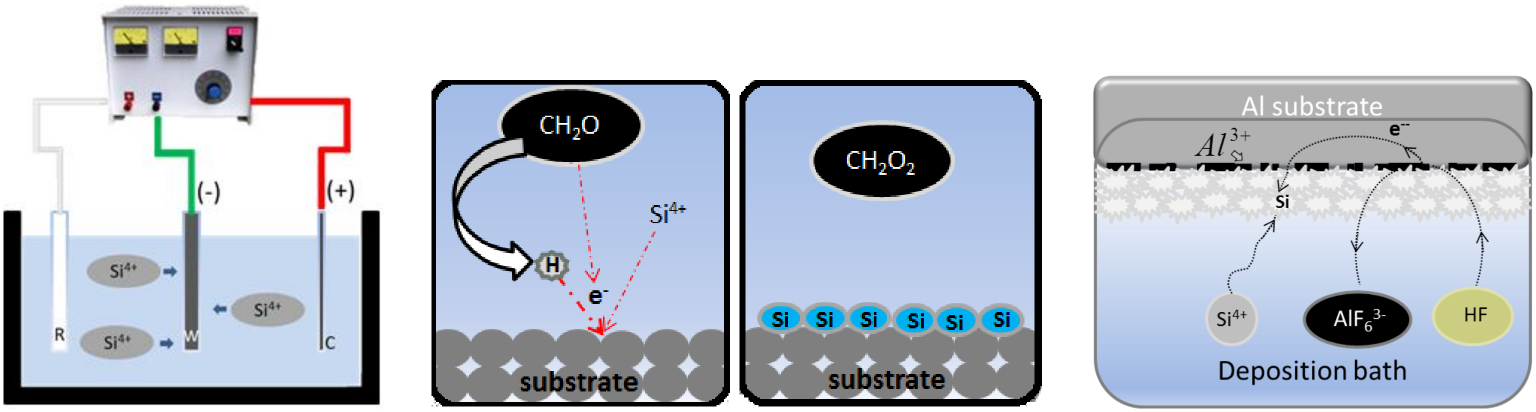


Figure 1. Periodic table of elements showing elements that can be electrodeposited from aqueous solution, with Al, semiconductors and refractory metals also indicated. Adapted with permission from reference #3.

In general, methods for electrochemical thin film deposition can be divided into three categories, depending on the electron source:

- Electrodeposition, where the electron source is an external power supply.
- Electroless deposition, where the electron source is a chemical reducing agent (i.e. formaldehyde, borohydride, hypophosphite).
- Galvanic deposition, where the electron source is the substrate itself, which is simultaneously oxidized and dissolved.

These methods for electrochemical deposition are illustrated in Scheme I, using Si as an example. Recent research into low temperature electrochemical deposition of the elements of interest has focused mainly on electrodeposition from room temperature ionic liquids, electrodeposition from organic solvents, and galvanic deposition from aqueous electrolytes.



$$Si^{4+} + 4e^- \rightarrow Si$$

$$CH_2O + H_2O \rightarrow CH_2O_2 + 2H + 2e^-$$
$$SiF_6^{2-} + 4e^- \rightarrow Si + 6F^-$$

$$Al + 6F^- \rightarrow AlF_6^{3-} + 3e^-$$
$$SiF_6^{2-} + 4e^- \rightarrow Si + 6F^-$$

(a) Electrodeposition (b) Electroless deposition (c) Galvanic deposition

Scheme I: Methods of electrochemical deposition

2. Electrodeposition from Room Temperature Ionic Liquids

Electrodeposition from room temperature ionic liquids, which have melting points <100°C, has been extensively investigated due to numerous advantages these solvents possess relative to high temperature molten salts, in which electrodeposition is typically performed at 500-1000°C [8]. These advantages include negligible vapor pressure (10^{-11} to 10^{-10} torr) at room temperature, which allows electrodeposition at elevated temperature without significant solvent loss; large electrochemical windows (~5 V), which allow electrodeposition of elements cathodic to the potential (~-0.83 V vs. NHE) at which water is reduced; reasonable electrical conductivity; and good thermal stability. Electrodeposition from ionic liquids provides an excellent starting point for discussion of state-of-the-art methods for low temperature electrochemical deposition due to the significant success reported for Al electrodeposition. Since the literature on electrodeposition from ionic liquids is voluminous, only recent publications are discussed here, with earlier studies discussed in previous reviews [9-11].

Due to the ubiquity of the Hall Heroult process in commercial Al smelting, Al electrodeposition from ionic liquids has been intensively studied. Early studies employed eutectic mixtures of an organic chloride salt with $AlCl_3$. These are easy to synthesize by addition of $AlCl_3$ to quaternary ammonium, imidazolium, or pyridinium chloride salts under an inert atmosphere [8]. The net reaction for Al electrodeposition is:

$$4Al_2Cl_7^- + 3e^- \rightarrow Al + 7AlCl_4^- \tag{1}$$

This reaction follows the electrochemical-chemical mechanism, so reaction (1) is the sum of:

$$Al_2Cl_7^- + 3e^- \rightarrow Al + AlCl_4^- + 3Cl^- \tag{2}$$

$$3Cl^- + 3Al_2Cl_7^- \leftrightarrow 6AlCl_4^- \qquad (3)$$

Recently, Endres and co-workers demonstrated that thick (~40 μm) Al coatings can be electrodeposited atop high-strength steel screws in an industrial production process from electrolytes containing 60 mol% $AlCl_3$ and 40 mol% 1-ethyl-3-methylimidazolium chloride at room temperature [12]. Al sheet and Al foil were used as the reference and counter electrodes, respectively. Al electrodeposition was performed in an Ar-filled glove box at an electrode potential of −0.3 V vs. Al/$AlCl_3$. The Al deposit morphology on the screw threads is illustrated in the scanning electron microscope (SEM) image of Figure 2.

The most difficult challenge encountered by Endres and co-workers was to obtain adequate coating adhesion, which required both carefully designed pre-treatment and post-treatment procedures [12]. An adhesive and corrosion-resistant Al film could be obtained only for steel screws that are first degreased by sonication, etched in HCl, plasma treated in an Ar/H_2 plasma, and then anodically etched in the ionic liquid. This complex pre-treatment is believed to be necessary for complete removal of all contaminants and the native oxide from the screw surface. Correct post-treatment is also required for an adequate Al coating. If the screw is rinsed with water in the ambient environment, hydrolysis products such as HCl attack the Al deposit, so the samples must be rinsed instead with 1-ethyl-3-methylimidazolium dicyanamide in an Ar atmosphere.

For low-strength screws, the same research group previously reported that a simpler pre-treatment procedure prior to Al electrodeposition from $AlCl_3$ in 1-ethyl-3-methylimidazolium chloride could be employed to ensure adequate adhesion [13]. Low-strength steel working electrodes were mechanically polished with emery paper, cleaned with acetone in an ultrasonic bath, immersed in dilute HCl, rinsed with distilled water, and immersed into dichloromethane for degreasing. However, without additional pre-treatment, Al deposit adhesion was quite poor due to reformation of a Fe oxide film. An additional pre-treatment step by in situ electrochemical etching dramatically improved adhesion of the Al deposit [13].

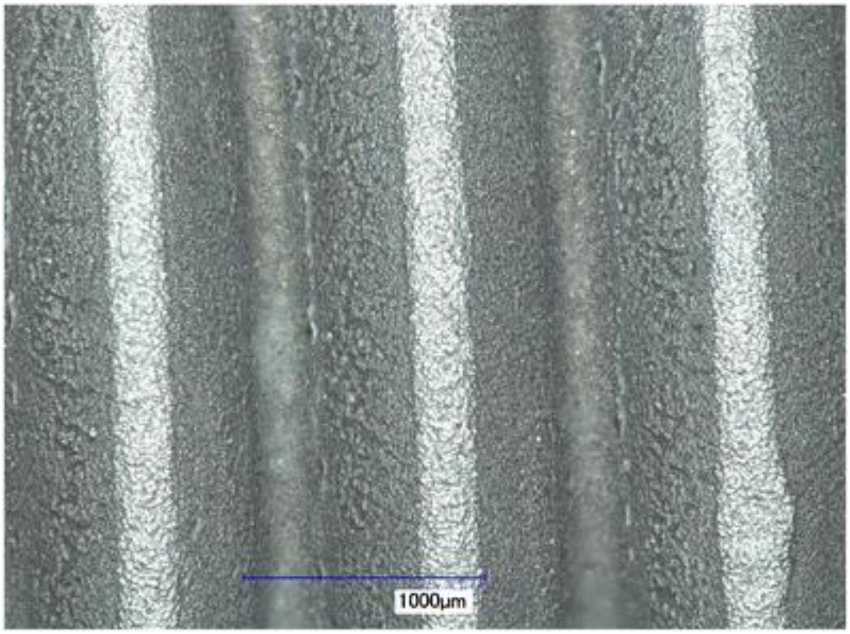


Figure 2. Microscope image of the threads on an Al-coated screw. Reproduced with permission from reference #12.

The autosolvolysis reaction (1) implies that electrodeposition of Al from acidic chloroaluminate salts should have a low current efficiency, since only 1/8 of the original Al source species are deposited. However, recent thermodynamic and kinetic modeling suggests that reasonable current densities can be attained due to the rapidity of reaction (3) [14]. In other words, the $AlCl_4^-$ species produced by reaction (1) rapidly reform $Al_2Cl_7^-$ by the autosolvolysis reaction (3) above. Early studies of Al electrodeposition from ionic liquids reported deposits that were rough, dull, and not very compact. One focus of recent research is on the addition of organic brightening agents such as 1,10-phenanthroline, toluene, ethylene glycol, and nicotinamide to ionic liquids for Al electrodeposition [15-18]. Similar to brighteners used during aqueous electrodeposition, this reduces the deposition rate but allows formation of smoother, brighter, and more compact deposits [15-18].

Although Al can be successfully electrodeposited from chloroaluminate ionic liquids, these solvents are quite hygroscopic. Al electrodeposition has also been reported from air and water stable ionic liquids that contain weakly coordinating anions with trifluoromethanesulfonyl (Tf_2N) groups [19], including several recent studies [20-22]. One of the complications of electrodeposition from ionic liquids in these systems is that the solvent species interact much more strongly with each other, with the reactant complex, and with the substrate. Endres and co-workers recently studied and compared Al electrodeposition from two different ionic liquids, $AlCl_3$ in 1-butyl-1-methylpyrrolidinium and trifluoromethylsulfonate [20]. Both yield Al electrodeposits of µm range thickness at 100 °C, but the former yields uniform Al coatings on Au and mild steel with an average grain size of 40-50 nm, while the latter yields coarse Al coatings with much larger (µm range) grain sizes. Such differences are often observed during electrodeposition from ionic liquids, and attributed to chemical interactions between solvent and the reactant complex, although these interactions are difficult to understand in detail. Rodopoulos and co-workers recently investigated chemical speciation in Tf_2N-based ionic liquids, and its effects on the kinetics and thermodynamics of Al electrodeposition [21,22].

Si electrodeposition from ionic liquids has been less successful than Al electrodeposition, since the maximum thickness attained to date for continuous Si films is ~1 µm. This has stimulated a range of studies to understand the mechanism of Si and Ge electrodeposition. As for Al, Si electrodeposition from different but related ionic liquids may yield quite different results. Si electrodeposition from $SiCl_4$ onto Au and Cu was recently studied from three different ionic liquids with the same cation, 1-butyl-1-methylpyrrolidinium, but three different anions, trifluoromethylsulfonate, bis(trifluoromethylsulfonyl)amide, and tris(pentafluoroethyl)-trifluorophosphate [23]. Cyclic voltammetry of all three electrolytes on Au are similar. However, nucleation of Si islands occurs at different potentials from these three electrolytes, and different features are observed for $SiCl_4$ stretching modes when FTIR spectra of $SiCl_4$ in these ionic liquids are obtained. These observations were attributed to different interactions of the $SiCl_4$ source with the three different anions [23]. Another recent study reported that during Si and Ge deposition from $SiCl_4$ and $GeCl_4$ dissolved in ionic liquids with the bis(trifluoromethylsulfonyl)amide (TFSA) anion, the deposit thickness fails to grow with time, and sometimes even shrinks [24]. This is ascribed to Si and Ge dissolution by the anodic decomposition products of TSA.

Another recent study of Si electrodeposition from trimethyl-n-hexyl ammonium bis-(trifluoromethylsulfonyl) employed an electrochemical quartz crystal microbalance and cyclic voltammetry, with the results suggesting both trapping of ionic liquid within the Si deposit, and incomplete reduction to Si(0) [25]. Another mechanistic study focused on color changes with time in both the electrolyte and Si-Ge deposits as evidence for the formation of solid particles within a 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-amide electrolyte [26-28]. A complex salt containing $GeCl_4$ in a mixed ionic liquid of 1-butyl-1-methylpyrrolidinium chloride ([BMP]Cl) and 1-butyl-1-methylpyrrolidinium dicyanamide was recently reported as an improved source for Ge electrodeposition, since this increases the solubility by about 13x [29]. This allows electrodeposition of smooth, porous Ge films of thickness ~1 µm.

Several studies have recently appeared on electrodeposition of refractory metals, including Ta [30-32], Mo [33], Nb [34-36], and Ti [37,38], from ionic liquids. Like Si, Ta electrodeposition from ionic liquids is quite challenging, with possible complications that may include incomplete reduction to Ta(0), porous deposits that may trap ionic liquids, and crack formation [30]. To date, the attainable Ta thickness is limited to less than ~1 µm. As for Al and Si electrodeposition, the quality of Ta deposits depends on the ionic liquid, and better results are generally obtained for Ta electrodeposition from TaF_5 than from $TaCl_5$ [30]. The mechanism of Ta electrodeposition is quite complex, and multiple reduction peaks are often observed during cyclic voltammetry, in part due to the stability of TaF_3. The tendency towards forming Ta sub-halides has been studied by electrochemical quartz crystal microbalance (EQCM), and sub-halide formation can be suppressed to some extent by Ta electrodeposition at higher temperatures [30].

Recently, two research groups reported Nb electrodeposition from ionic liquids at about the same time [35,36]. Endres and co-workers reported that Nb coatings ~1 µm thick can be electrodeposited onto Au or Cu from electrolytes containing NbF_5 and LiF in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide at 170°C [35]. Similar to the case for Ta electrodeposition, some incorporation of sub-fluorides is observed, with their presence reduced as the temperature is increased. The addition of either LiF or Li bis(trifluoromethylsulfonyl) amide was required in order to obtain reasonable adhesion to the substrate [35]. Vacca and co-workers reported Nb electrodeposition from the same ionic liquid at 125°C in the presence of LiF [36]. Results from cyclic voltammetry and energy dispersive x-ray spectroscopy (EDX) suggest a complex reaction mechanism through intermediate carbide phases [36].

Ti electrodeposition from ionic liquids provides an even greater challenge than Ta or Nb [37,39]. Reduction of $TiCl_4$ or TiF_4 to Ti metal does not appear to be feasible in a variety of different ionic liquids due to several interrelated complications: incomplete reduction of Ti(IV), formation of insoluble and poorly conductive Ti halides on the substrate, and reactions of Ti complexes with the solvent [37,39]. To circumvent this limitation, Ti electrodeposition from TiO_2 precursor was recently reported from a Lewis basic mixture of $AlCl_3$ and 1-butyl-3-methylimidizolium [38]. Although voltammetry studies suggested that Ti(IV) can be reduced to metallic Ti, the reaction rate was quite slow, and only 12 wt% of TiO_2 had reacted after 48 hr. To date, continuous, µm-scale Ti coatings from have not been successfully electrodeposited from ionic liquids.

The main advantages of ionic liquids as solvents for electrodeposition are their low vapor pressures and wide electrochemical windows. For the highly active elements considered here, the critical advantage of ionic liquids is that oxidation, which occurs rapidly in aqueous electrolytes, is much more easily prevented. The main disadvantages of ionic liquids are their toxicity and high cost, and the complex interactions between cations, anions, reactant complexes, and the substrate onto which the coating is formed. In addition, some ionic liquids and elemental sources (i.e. $AlCl_3$) are quite sensitive to the presence of even trace quantities of O_2 and H_2O. Of the elements considered here, thick, continuous and adherent deposits have been attained for Al, while for other systems some challenges remain. The formation of rough, island, and porous deposits may be difficult to avoid when using ionic liquids, although in the case of Al electrodeposition, effective brighteners have been identified.

3. Electrodeposition from Organic Electrolytes

Two commercial processes are available for Al electrodeposition from organic solvents: a process developed by Siemens with alkylaluminum compounds dissolved in toluene, which operates at 100°C; and a process developed by Philips with $AlCl_3$ and $LiAlH_4$ dissolved in tetrahydrofuran [12]. The only recent literature on Al electrodeposition from organic solvents studies the $AlCl_3$ dimethylsulfone electrolyte [40,41]. Dimethylsulfone has the advantage of being much less expensive than room temperature ionic liquids, and yet more stable and less volatile (boiling point = 238°C) than other organic solvents, such as ethers and aromatic hydrocarbons, which are sometimes employed for electrodeposition from organic solvents. In dimethylsulfone ($DMSO_2$), Al electrodeposition can occur from the solvated cation that forms by the following reaction:

$$4AlCl_3 + 3DMSO_2 \rightarrow Al(DMSO_2)_3^{3+} + 3AlCl_4^- \qquad (4)$$

Electrochemical reduction of $Al(DMSO_2)_3^{3+}$ can then occur within the electrochemical window of dimethylsulfone, whereas reduction of $AlCl_4^-$ is outside the electrochemical window of most electrolytes. Hirato and co-workers recently demonstrated that addition of trimethylamine hydrochloride to $AlCl_3$-$DMSO_2$ electrolytes reduces the extent of incorporation of Cl and S impurities, probably due to electrostatic effects at the coating surface [40]. The inclusion of Cl and S impurities makes the Al electrodeposit hard and brittle, and also reduce its corrosion resistance. This research group also studied a series of polyethylene amines as brighteners for Al electrodeposition from $DMSO_2$, obtaining the best results for triethylenetetramine at a wide range of current densities [41].

Similar to ionic liquid electrolytes, Si electrodeposition is more challenging than Al electrodeposition from organic solvents. Two recent studies of Si electrodeposition have appeared from different organic solvents [42,43]. In both cases, the Si source was $SiCl_4$ and tetrabutylammonium chloride and tetraethylammonium chloride were used to increase the electrolyte conductivity [42,43]. Bechelany and co-workers report a detailed study and comparison of Si electrodeposition from acetonitrile and dichloromethane, and report film thicknesses up to 5-7 µm [43]. Si electrodeposition was most successful from acetonitrile, which yields a much more compact deposit with much less carbon incorporation. Raman spectra that demonstrate deposition of amorphous Si, with a broad peak near 490 cm^{-1} were observed, as shown in Figure 3. The peaks at 415, 626, and 665 cm^{-1} in Figure 3 were assigned to the F-doped, SnO_2-coated glass substrate [43]. In these studies, particular care was taken to limit oxygen exposure, including electrodeposition in a Schlenk-type flask in an Ar atmosphere, and the use of non-oxygenated solvents for both electrodeposition and rinsing.

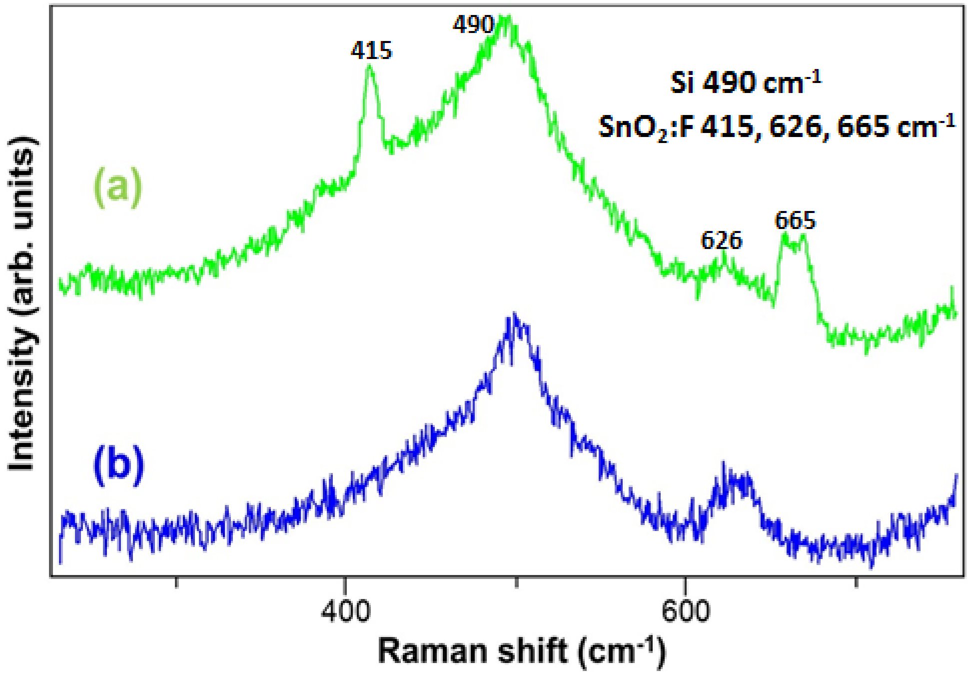


Figure 3. Raman spectra of Si deposit from acetonitrile (a) and dichloromethane (b). Reproduced with permission from reference # 43.

The most significant advantages of electrodeposition from organic solvents are that they are considerably less expensive and more stable than ionic liquids. Thus electrodeposition from organic baths is less expensive. The most significant disadvantage is the flammability and volatility of organic solvents, and the toxicity of some of the compounds employed. This results in both significant safety concerns and problems with bath replenishment. In addition, coatings formed by electrodeposition from organic solvents often contain impurities that make then hard and brittle.

4. Electrodeposition and Subsequent Precipitation onto a Liquid Metal Cathode

Maldonado and co-workers recently reported low temperature electrodeposition of Ge and Si by an electrochemical liquid−liquid−solid (ec-LLS) process [44,45]. This involves electrodeposition atop a liquid metal cathode in which the deposit is sparingly soluble, convection-diffusion of the deposited element into the near-surface region of the cathode, and eventual precipitation of the deposit from this solution when it reaches supersaturation. In other words, the liquid metal cathode is used as a separate phase for recrystallization. The ec-LSS process has been demonstrated for Ge electrodepositon on an Hg cathode from an aqueous solution of 50 mM GeO_2 and 10 mM $Na_2B_4O_7$ at pH 8.5 and room temperature [44], and for Si electrodeposition from 0.5 M $SiCl_4$ and 0.2 M tetrabutylammonium chloride in propylene carbonate on a liquid Ga cathode at 80-100°C [45]. The solubility of Ge in Hg is only $2x10^{-7}$ M, while the solubility of Si in Ga extrapolated from metallurgical data is in the range 10^{-6} to 10^{-4} M. This novel approach has been demonstrated for both aqueous and organic electrolytes, and thus merits separate consideration here.

No cathodic peaks are observed during cyclic voltammetry of Ge or Si precursors, but increased cathodic current is clearly observed in their presence, as illustrated in Figure 4 [45]. Two anodic peaks at ~0.0 and -0.5 V vs. Ag/AgCl can be attributed to Ge oxidation, as previously observed during polarography of Ge films. Surprisingly, Ge electrodeposition onto Hg has a much higher current efficiency than on other substrates such as Cd and Zn where H_2 is also kinetically sluggish [44].

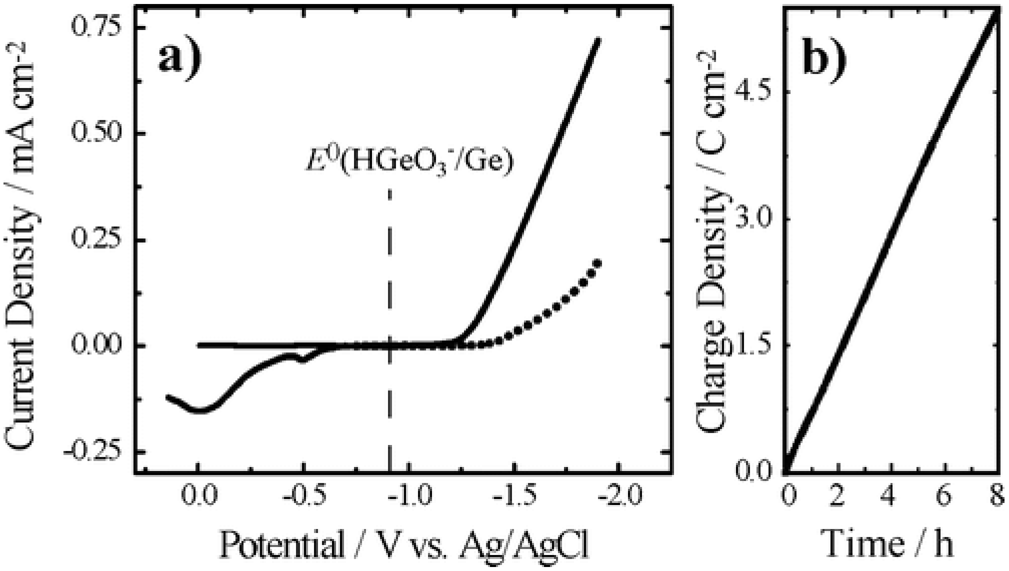


Figure 4. Voltammetric response at an Hg cathode in deaerated 10 mM $Na_2B_4O_7$ without (dotted line) and with (solid line) 50 mM GeO_2 at a scan rate of 10 mV/s. Reproduced with permission from reference #44.

Depending on the potential, Ge deposits range from a dense leaf-like structure to three-dimensional mats of Ge filaments, with the mat thickness reaching ~10 µm after two hours of deposition [44]. X-ray diffraction is consistent with diamond phase Ge crystallites with a diameter ranging from 8-53 nm. The smallest size is obtained at potentials less than -1.9 V vs. Ag/AgCl, probably due to enhanced nucleation at highly cathodic potentials [44]. Si deposits appear to be agglomerated particles, but no thickness is provided for continuous film formation [45]. X-ray diffraction indicates diamond phase Si crystallites with diameters greater than 100 nm. Formation of Si rather than SiO_2 is verified by experiments at different temperature, and comparison of results with and without annealing, which demonstrate that only deposition performed at high temperature yields a deposit that retains its dark color indefinitely in an ambient environment. Gradual color change from dark grey to white has long been used to indicate formation of porous Si that gradually oxidizes to SiO_2 [46].

The electrochemical liquid−liquid−solid (ec-LLS) process for Ge and Si electrodeposition demonstrates deposition of crystalline deposits at much lower temperatures than previously reported [44,45]. Previous reports of Si electrodepositon from electrolytes containing $SiCl_4$ in propylene carbonate yield only amorphous Si [47,48]. The results of Maldonado and co-workers are quite promising and recent, so the full potential of these methods is still unknown. However, electrodeposition of thick, dense and continuous Si and Ge thin films still appears to be challenging. For the case of Si, organic solvents may still be needed.

5. Galvanic Deposition from Aqueous Electrolytes

As illustrated in Scheme I, galvanic deposition can be employed for electrochemical thin film growth through reduction and deposition of a more noble element from the solution phase, accompanied by simultaneous oxidation and dissolution of a more active element from the substrate. Galvanic deposition provides the simplest and least expensive method for electrochemical thin film deposition, since this process involves simply immersing the substrate into the deposition bath, with no potential/current source required. However, applications of galvanic deposition have been modest due to several shortcomings, including difficulty in controlling deposition, since this occurs spontaneously without application of an external potential, and substrate consumption, which often leads to limited adhesion. The most common applications of galvanic deposition include Pd coatings for improved corrosion resistance [49], Au coatings atop Ni for surface preparation [50], and Zn coatings to prepare Al for subsequent Cu or Ni deposition [51]. However, galvanic deposition of active elements has only recently been reported.

We recently reported galvanic deposition of compact Ti and Mo [52,53], galvanic deposition of nanoporous Si [54], and galvanic/electroless deposition of compact Si films [55], all deposited on Al alloy substrates. This approach takes advantage of the fact that Al is one of the most active elements, so quite active elements can be noble to Al when present in an electrolyte. For the case of Ti and Si, the electrolyte solution from which they are deposited must contain fluoride ions to prevent native oxide formation. Deposition of compact Si films > 5 μm thick were reported from formic acid electrolytes [55]. In this system, the electrochemical half-reactions that occur are most likely [7]:

$$SiF_6^{2-} + 4e^- \rightarrow Si + 6F^- \qquad E^0 = -1.37V\ vs.\ NHE \tag{5}$$

$$AlF_6^{3-} + 3e^- \rightarrow Al + 6F^- \qquad E^0 = -2.07V\ vs.\ NHE \tag{6}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H \qquad E^0 = -0.20V\ vs.\ NHE \tag{7}$$

Reaction (7) is oxidation of formic acid, so this Si coating process is a combined galvanic/electroless deposition method. Both anodic reactions, which are the reverse of reactions (6) and (7), are important during Si deposition, due to the following observations. In formic acid electrolytes atop noble substrates (i.e. Cu and Au), no Si coating is obtained. For aqueous electrolytes that do not contain formic acid, only nanoporous deposits can be obtained atop Al alloy substrates [54]. Thermodynamically, Al is a much stronger reducing agent than formic acid. However, oxidation of formic acid may become kinetically favored as the Si film thickness, and the distance between the Si surface and the underlying Al substrate increases.

For Ti deposition, the following electrochemical half-reactions are most likely [52]:

$$TiF_6^{2-} + 4e^- \rightarrow Ti + 6F^- \qquad E^0 = -1.91V\ vs.\ NHE \tag{8}$$

$$AlF_6^{3-} + 3e^- \rightarrow Al + 6F^- \qquad E^0 = -2.07V\ vs.\ NHE \tag{9}$$

Chemical speciation in $MoCl_5$-containing electrolytes is complex, so electrochemical half-reactions during galvanic Mo deposition are uncertain [53]. Since Al oxidation (reactions 6 and 9 above) is integral to galvanic deposition, Ti, Mo and Si deposition are all coupled to Al dissolution and transport through the growing thin film coating. Thus Al contamination is intrinsic to these galvanic deposition methods, yielding deposits that contain ~90 atom% Ti, 82 atom% Mo, and 93 atom% Si, as measured by EDX. H_2 evolution is observed to a varying extent during Ti, Mo and Si deposition [52-55], and some hydrogen incorporation into these deposits is likely.

Much of the evidence cited for galvanic deposition of compact and elemental Ti, Mo and Si from aqueous electrolytes is indirect [52,53,55], based on color retention during prolonged exposure to ambient air, film resistivity measurements by four-point probe, and the ability to perform electrochemical measurements through thick (5-10 µm) coatings. As noted earlier, gradual color change from dark grey to white has long been used as evidence for a porous Si deposit [46]. Nevertheless, it is difficult to completely exclude the possible formation of sub-oxides, or other species not completely reduced to zero valence. However, in the case of Ti deposition, polycrystalline Ti deposits of grain size ~20 µm are indicated by the x-ray diffraction results shown in Figure 5 [52]. In addition, F incorporation and/or Ti film porosity is observed when the pH is varied away from the optimal range of 2.6-3.0, providing further evidence for deposition of compact, elemental Ti is optimized in that pH range.

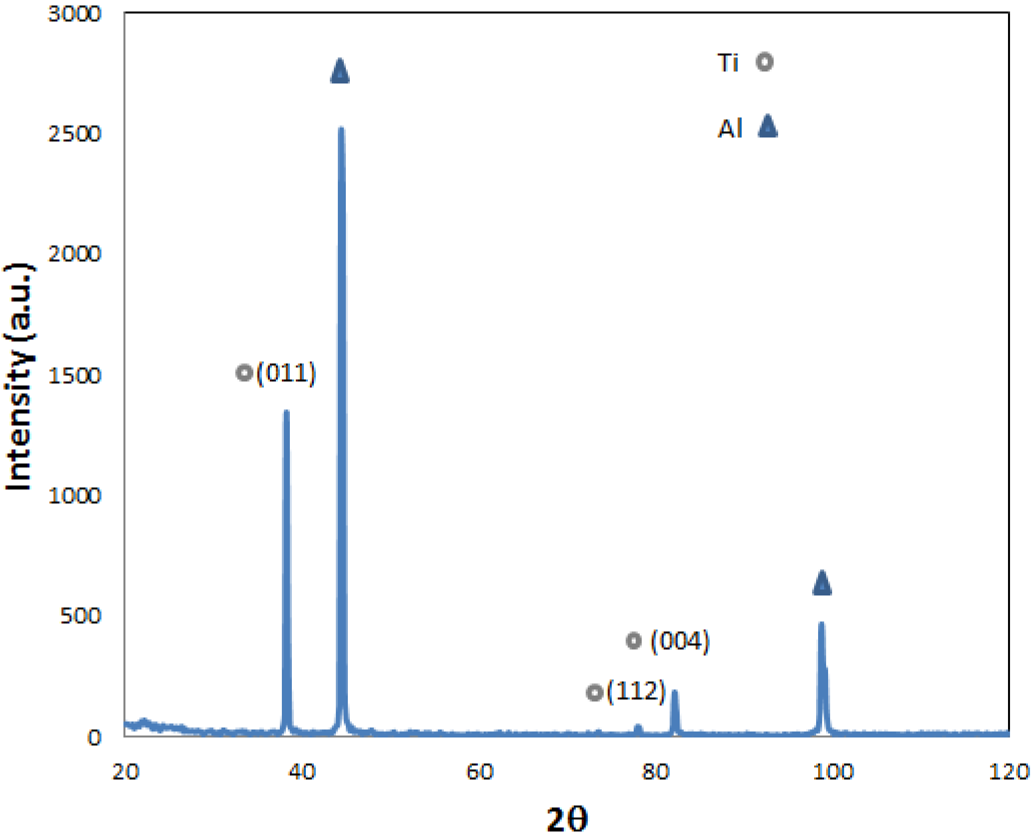


Figure 5. X-ray diffraction pattern of Ti film deposited atop Al 6061 alloy from 17 mM HF and 10 mM K_2TiF_6. Reproduced with permission from reference #52.

Galvanic deposition of Ti and Mo, and electroless/galvanic deposition of Si, have only been reported to date upon Al alloys. During galvanic deposition, complications may arise from the interrelated issues of alloying elements present in the substrate, deposit nucleation, surface roughness, and coating adhesion. For the case of galvanic/electroless Si deposition onto pure Al, Si deposits still form, but flake off immediately [55]. Adequate adhesion could only be obtained for galvanic/electroless Si deposition atop Al alloy substrates, where certain impurity elements appear to anchor the depositing film. Adherent Si deposits were only obtained on some Al alloys, but these effects were not studied systematically. Such substrate dependence during galvanic deposition is not uncommon. For example, galvanic Zn deposition was recently reported to proceed with much better nucleation atop Cu-containing Al than atop Si-containing Al alloys [56]. This observation was attributed to electrocatalytic activity of Cu nuclei towards Zn reduction. Quantitative studies of adhesion strength for electroless Ni-P deposits atop zincate-treated Al alloy suggest that both nucleation and adhesion depend in a complex manner upon the presence of different alloying elements [57].

Inguanta and co-workers recently employed the same Si deposition chemistry reported above using a galvanic cell constructed with a nanoporous polycarbonate membrane to separate the cathodic and anodic reaction sites [58]. With this arrangement, pure Si was deposited within the polycarbonate nanopores, resulting in formation of Si nanotubes. The authors attributed the formation of Si nanotubes rather than nanowires to gas bubble evolution that prevents closure of the template nanopores [58]. After dissolution of the polycarbonate membrane in dichloromethane, they obtained Si nanotube bundles with an average length of 18 µm and wall thickness of 38 nm. Deposition of compact, amorphous Si was supported by Raman spectroscopy, with a broad band from 480-540 cm^{-1} characteristic of amorphous Si. In addition, photoelectrical measurements showed n-type conductivity and an optical band gap of ~1.6 eV, in agreement with literature values. A galvanic cell with a similar geometry constructed using a nanoporous alumina membrane was recently employed by Inguanta and co-workers for galvanic deposition of different lanthanide elements (La, Ce, Sm, Er), which immediately reacted with the electrolyte to form lanthanum oxides and/or hydroxides [59].

The biggest advantage of the galvanic deposition processes discussed here are their cost and simplicity, since these simply involve immersion of an Al substrate into an aqueous electrolyte. In addition, thick deposits can be easily obtained, despite the common misconception that galvanic deposition is self-limiting after one monolayer of deposition. The biggest disadvantages are the difficulty in controlling the reaction rate, and the coupled issues of substrate consumption and film adhesion. These methods are restricted to Al and other highly active metals.

6. Conclusions

Electrodeposition from room temperature ionic liquids has been intensively studied during the last two decades. Al electrodeposition from acidic chloroaluminate salts is relatively mature, and Al coatings up to 40 µm have been reported. The main limitations for commercial usage are the toxicity and high cost of the ionic liquids, and the complexity of excluding O_2 and H_2O in a manufacturing environment. Electrodeposition of Si, Ta and Nb from ionic liquids has also been reported, but coating thickness is limited to date to ~1 µm. Ti electrodeposition from ionic liquids has not yet yielded continuous coatings due to incomplete reduction of Ti(IV), formation of insoluble and poorly conductive Ti halides on the substrate, and reactions of Ti complexes with the solvent. Electrodeposition from organic solvents provides a simpler and less expensive alternative to ionic liquids, but applications have been limited by the flammability and volatility of organic solvents, which raise significant safety concerns and require frequent bath replenishment. Nevertheless, Al electrodeposition from dimethylsulfone, which is more stable and less volatile than many other organic electrolytes, has shown promise, with recent studies demonstrating that the addition of additives can reduce deposit contamination and improve deposit quality. Si electrodeposition from organic solvents has also recently been demonstrated as potentially viable. The electrochemical liquid−liquid−solid (ec-LLS) process for Ge and Si electrodeposition recently reported by Maldonado and co-workers demonstrates deposition of crystalline deposits at much lower temperatures than previously reported. Galvanic deposition is the simplest and least expensive electrochemical method discussed herein. In addition, thick deposits of several active elements onto Al alloys have been recently reported. Commercial practice of galvanic deposition requires detailed understanding of particular systems of interest in order to address the coupled issues of substrate consumption and film adhesion.

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