Current Opinion in Solid State and Materials Science 19 (2015) 77–84

Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

journal homepage: www.elsevier.com/locate/cossms

Low temperature electrochemical deposition of highly active elements

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ARTICLE INFO

Article history:
Received 20 June 2014
Revised 24 November 2014
Accepted 28 November 2014
Available online 16 December 2014

Keywords:
Electrodeposition
Electroless deposition
Galvanic deposition
Ionic liquids
Organic electrolytes

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.

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.

Fig. 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

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http://dx.doi.org/10.1016/j.cossms.2014.11.006
1359-0286/

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
$SiF_6^{2-} + 4e^- \rightarrow Si + 6F^-$	−1.37
$Ti^{2+} + 2e^- \rightarrow Ti$	−1.63
$Al^{3+} + 3e^- \rightarrow Al$	−1.67
$AlF_6^{3-} + 3e^- \rightarrow Al + 6F^-$	−2.07

Al, semiconductors Si and Ge, and the refractory metals are all indicated in Fig. 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 1900 °C (3500 °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.

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 1, 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.

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}–10^{-10} torr) at room temperature, which allows electrodeposition at elevated temperature without

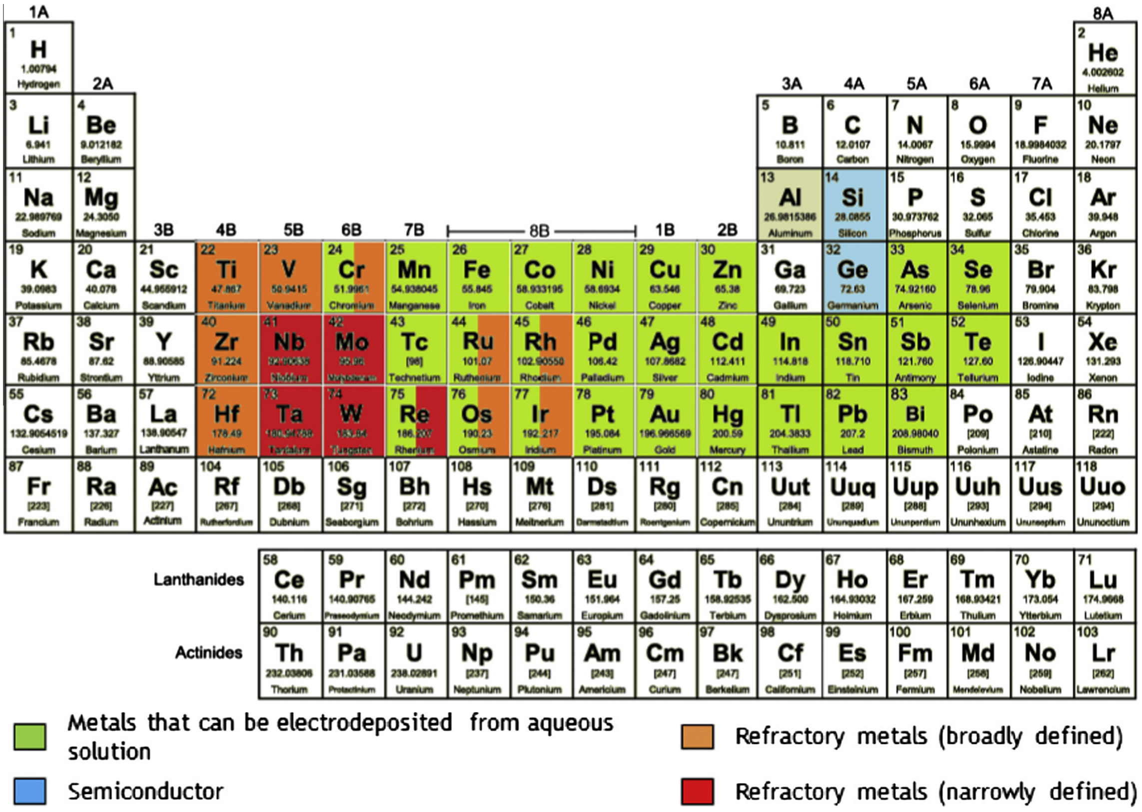

Fig. 1. Periodic table of elements showing elements that can be electrodeposited from aqueous solution, with Al, semiconductors and refractory metals also indicated. Adapted with permission from Ref. [3].