Electrochemical deposition of silver and copper from a deep eutectic solvent studied using time-resolved neutron reflectivity

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ABSTRACT

Here, we describe new developments in the study of electrodeposition processes with time-resolved dynamic neutron reflectivity (NR) methods to achieve insights into the differences between growth of metal films using a range of electrochemical control functions. We show that the temporal resolution has increased from 1 to 2 h per data set (in our previous studies) to approximately 8 min. We have studied the electrochemical deposition of copper and silver as thin-film metals onto a gold electrode substrate from a deep eutectic solvent using potentiodynamic (PD), potentiostatic (PS) and galvanostatic (GS) electrochemical control functions. In particular, we have utilised novel developments in neutron reflectivity methods to acquire real-time data for the growing metal films. *Event mode* capture of neutron scattering events, as a function of momentum transfer vector, Q, during electrochemical growth has enabled time-resolved measurement of the neutron reflectivity, $R(Q)$, profiles of the growing metal films. Subsequent fitting and iterative optimisation of the $R(Q,t)$ data reveals the thickness, roughness and relative density (spatially resolved solvent content) of the metal film during growth. These data show that the different electrochemical growth methodologies exhibit different trends in thickness, roughness and solvation. Silver films show an increasing roughness trend with time but these trends are largely independent of growth method. In contrast, the roughness of copper films, grown under similar conditions, shows a strong dependency on growth method with PS methods producing smoothest films. These conclusions are confirmed by *ex-situ* AFM measurements. The fitted NR data show that the Cu and Ag films contain between 5 and 10% volume fraction solvent. Furthermore, we have explored different NR data fitting methodologies in order to process the large numbers of data sets produced. Gratifyingly, the different methodologies and starting conditions yield a very consistent picture of metal film growth.

1. Introduction

Electrodeposition of metal films and coatings is a core practice for a variety of high technology and manufacturing industries. The range of metals of interest is very wide and includes Cr, Ni, Cd, Cu, Zn and Sn, for anti-corrosion and wear coatings used in automotive, aerospace and many other industries. Au, Ag and Pt, are important for electronics fabrication and manufacturing and Al, Li, Na, Co and Mn for energy storage applications, including novel batteries. In many applications, it is necessary to control the physical properties, morphology, roughness, and density of the metal film produced by electro-reduction of metal

ion. This is particularly the case where thin films are required. Such technologies include electronics fabrication and manufacturing, including printed circuit boards (PCB). In the latter case multi-layer thin films of, for example, Ni, Cu, Ag, Au and others are often produced by electrolytic reduction.

The overwhelming majority of electrolytic metal processing is carried out in water based solutions. However, despite their maturity, aqueous deposition processes still possess significant limitations such as low current efficiency, coating embrittlement and dendrite formation; stringent process control is often necessary to maintain specification which leads to bath complexity and rigorous maintenance requirements

[1]. In addition, strong inorganic acids and bases are often needed and the metal salts required, for example cyanides, are often very toxic. Consequently, the use of novel ionic liquid [2] (IL) media and in particular deep eutectic solvents [3] (DES) is gaining attention. DESs are systems formed from eutectic mixtures of Brønsted or Lewis acids and bases, typically mixtures of the salt choline chloride with small hydrogen bonding molecules such as ethylene glycol or urea [3]. DES based electrolytes have been used for the electrodeposition of a wide range of metal and alloy coatings including Cu [4,5], Sn [6–8], Zn [9,10], Cr [11,12], Zn/Ni [13] and Zn/Sn [14]. These DES electrolyte media offer prospective improvements in process control/efficiency, environmental sustainability/impact and functionality as well as giving access to reactive metal deposition not previously possible (for example Al). In addition, due to the fundamental differences between molecular solvents like water and ILs/DESs there are significant disparities in the way metal films nucleate and grow on surfaces [15].

Electrochemical reduction is driven by control of either the applied potential, E_{App}/V, or the current density, i/A cm^{-2}. Since one is a function of the other there are two generic methodologies for deposition of a metal film; these are potential control and current control. Potential control is achieved most simply by applying a fixed value of cathodic potential sufficient to drive the reduction process. In this case the resultant current density varies with time, $i(t)$, according to the availability of metal ion species and/or the rate of limiting kinetic factors (heterogeneous electron-transfer, metal complex ligand exchange *etc.*). This is the potentiostatic method (PS) and here the thermodynamic driving force, E_{App}, is constant but the rate of reaction, i, is (in general) a function of time. Alternatively, current control is achieved by driving a fixed value of current through the cell in the direction of the reduction reaction. In this case the value of applied potential required to sustain the chosen current will vary with time for the same reasons (above). This is the galvanostatic method (GS) and here the rate of reaction, i, is fixed but the driving force, E_{App}, is a function of time.

During PS deposition, the rates of nucleation and growth of the metal film are determined by the fixed overpotential. This often results in control over the nucleation mechanism and possibly grain size/structure but can lead to very slow deposition rates at long experimental time scales. In contrast, GS methods offer control of reduction rate but this can lead to large variations in applied potential and current efficiency which, in turn, can cause roughness due to the variation in nucleation and growth kinetics. A third option is to gradually sweep the applied potential in the cathodic direction from a starting, quiescent, potential through the kinetically controlled region of the voltammetric reduction peak to a final value in the diffusion controlled region. This is a potentiodynamic (PD) (linear sweep voltammetry) method. Sweeping the potential in this way offers control of the initial nucleation conditions, at low rate, but then increases the rate of deposition at longer times through gradual, but controlled, increases of the applied potential. In this way the PD method combines some of the attractive features of both the PS and GS methods.

Each of these three methods of electrolytic growth can produce coatings with different physical attributes because of the limiting conditions under which growth is maintained. Consequently, a detailed understanding of how these control functions influence the structure and properties of the growing metal film is critical to being able to reproduce consistent metal films to a prescribed thickness and specification.

We have been engaged in the study of electrolytic metal deposition and dissolution in DES media in relation to potential applications in the aerospace and electronics manufacturing sectors [16]. Here it is important to be able to control and predict rate of deposition of the metal as well as to achieve target values of surface roughness and coherent, dense coatings. Monitoring thickness, surface roughness and density during electrodeposition can be achieved by a combination of techniques including electro-gravimetry (Quartz Crystal Microbalance, QCM)

[17], holographic imaging (Digital Holographic Microscopy, DHM) [18], scanning electron microscopy (SEM), optical profiling [19] and scanning probe microscopy (Atomic Force Microscopy, AFM) [20] as well as integrated electrochemical techniques (chronocoulometry). Each of these techniques has individual strengths but cannot in isolation deliver the necessary insights and metrology. Electrochemical and QCM measurements have good temporal resolution but are averaged over the sample volume (both across the surface and throughout its depth). Optical microscopy is limited by line of sight access to the electrode surface and the spatial resolution of visible wavelengths, whereas high resolution techniques such as SEM can only be utilised *ex-situ*. Probe microscopy can offer great insight into the shape of an evolving surface during growth [21] and into the mechanism of growth, but the proximity of the sharp probe close to the electroactive interface, or touching it, can initiate nucleation events and thus perturb the measurement. Furthermore, none of these techniques is capable of quantifying the internal composition of the deposited film during deposition.

An alternative is to use neutron reflectivity, NR, techniques [22]. This approach has many similarities to optical ellipsometry although the metal coatings here are optically opaque and so ellipsometry is not appropriate. Neutron reflectivity techniques are able to provide not only thickness and roughness data for the growing film but also compositional detail perpendicular to the plane of the electrode *i.e.* in the direction of growth. Development of NR methods to study "buried" interfaces under electrochemical control has distinguished composite and bilayer polymer films [23], revealed permeating solvent in electroactive polymer [24] and metal hydroxide [25] films, identified permselectivity failure at high electrolyte concentration [26], and revealed 1D profiling of diffusion and reaction within a film of a solution phase mediator [27]. Of relevance here, we have used a combination of *in-situ* techniques including NR to evaluate the influence of electrolytic deposition conditions on the solvation of reactive conducting polymers [28,29]. These and related [30,31] NR studies have data acquisition time scales of 1–2 h per acquisition, so the equilibrated films can be observed, as a function of potential and/or charge, but not the dynamics of interconversion.

In previous studies, we have been able to achieve better effective temporal resolution by signal averaging over repetitive scans and have reported the first dynamic electrochemical NR measurements by repetitive scan voltammetry [32]. This enabled the study of the time and potential dependent thickness and solvation of a poly(vinyl ferrocene) film. However, that strategy is inappropriate for 'single-shot' experiments. More recently, developments in instrument technology and data processing at the ISIS neutron and muon source, Rutherford Appleton Laboratory, have resulted in greatly improved temporal resolution. Data capture in *event mode* allows monitoring and recording of individual neutron events. This enables the combination (statistical averaging) of neutron data, post-acquisition, over a flexible, user-defined time scale. The subsequent time scale required for a single $R(Q)$ profile can be as little as tens of seconds in principle (*cf.* 1–2 h earlier), however, the cost of increasing temporal resolution is increased signal:noise (in R and Q). A crucial advantage of the *event mode* experiment is that it offers the capability to process all the acquired data *after* the experiment (without introducing dead time during data acquisition). This provides flexibility in achieving the desired balance of temporal resolution and noise and removes ambiguities associated with sample relaxation during interrupted measurements. We have recently exploited these new developments to study the electrochemical NR dynamics of both metal deposition and conducting polymer growth [33].

Here we have achieved good signal to noise in the NR data at temporal resolution of typically 5–10 min but varying to suit experimental needs. *Event mode* capture of synchronous neutron scattering events during electrochemical growth has enabled time-resolved measurement of the neutron reflectivity profiles of the growing metal films.