In Situ Stress Measurements During Aluminum Deposition from AlCl$_3$–EtMeImCl

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Electrodeposited films tend to develop sizable mechanical stresses as a result of the nucleation and growth process or from the use of solution additives and alloying elements needed to achieve desired deposition rates and mechanical properties. Often these stresses can approach or exceed the yield stress of the bulk material and can lead to loss of adhesion and the generation of bulk and surface defects. The electrodeposition community has been keenly interested in residual stress and its measurement [1]. It has recently been shown that the growth stress that develops in copper films electrodeposited from aqueous sulfate electrolyte is very similar to that which has been reported for Cu deposition from the vapor phase. The stress development in Cu is typical of high-mobility Volmer-Weber growth [2]. The general observation is that the stress progresses from compressive to tensile and then back to compressive (referred to as CTC behavior). The initial compressive stress occurs in the discrete-nuclei stage of growth and is due to the surface stress of these small particles. The rapid development of tensile stress is associated with nuclei coalescence and grain boundary formation while the final compressive stage occurs during thickening of the continuous film. The purpose of this paper is to examine the stresses associated with the earliest stages of aluminum deposition from an ambient temperature molten salt.

In situ stress measurements were made on a HeNe optical bench using the wafer curvature method during aluminum electrodeposition from the ambient-temperature Lewis acidic AlCl$_3$–1-ethyl-3-methylimidazolium chloride (AlCl$_3$–EtMeImCl) molten salt. The substrate was a 60 mm x 3 mm x 0.1 mm wafer of borosilicate glass onto which 250 nm of Au was evaporated. The electrode was flame-annealed, leaving the Au with a (111) crystallographic texture. The curvature of the substrate was monitored during electrodeposition by reflecting the laser off of the glass/metal interface, through a series of mirrors and onto a position-sensitive detector. The relationship between the force (F) per cantilever beam width (w) exerted by the electrodeposit and the radius of curvature of the cantilever is given by Stoney's equation [3]. The electrolyte was a 55-45 mole ratio of AlCl$_3$–EtMeImCl. The counter electrode was an aluminum wire placed parallel to and in the same solution as the working electrode. The reference electrode was also an aluminum wire placed in the same solution as the working and positioned between the working and counter electrodes.

Figure 1 shows the linear sweep voltammetry as well as the surface stress for the underpotential deposition (upd) of Al onto (111)-textured Au. The voltammetry shows a single cathodic peak at 0.165 V and two anodic peaks at 0.24 V and 0.45 V. Integration of the single cathodic peak results in a charge of about 725 mC/cm^2 which corresponds to a fully discharged monolayer of Al on Au. This is somewhat different from reports in the literature which show several cathodic processes which are attributed to both aluminum UPD and Al-Au alloy formation [6-8]. When the potential of the Au electrode is decreased from 0.8 V to 0.3 V, the surface stress (F/w) decreases slightly in the compressive direction. A significant tensile stress is associated with the cathodic upd process at 0.165 V. The stress continues to increase until the first anodic wave occurs, after which the stress returns to its original value.

Figure 2 shows the F/w associated with the bulk deposition of aluminum for a film thickness up to 0.13 μm. The negative force indicates that the Al films develop a compressive stress in the earliest stages of deposition. The compressive stress is also seen to increase with deposition overpotential. Interestingly, the high overpotential deposits develop a tensile stress as deposition continues. The thickness at which this occurs depends on the deposition overpotential. Possible growth mechanisms that contribute to this stress development will be discussed.
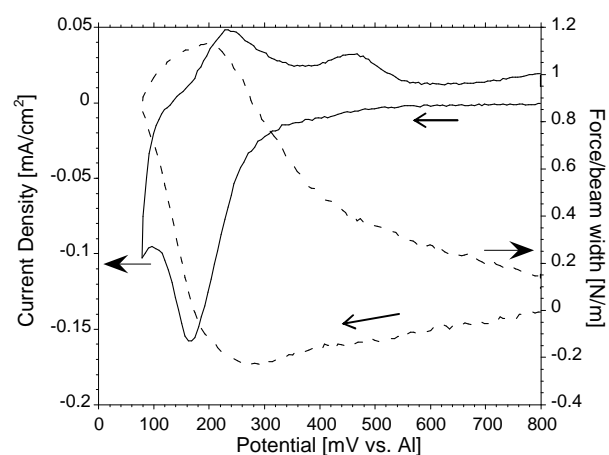

Figure 1. Linear sweep voltammetry (——) and surface stress (----) associated with the underpotential deposition of Al onto (111) - textured Au.
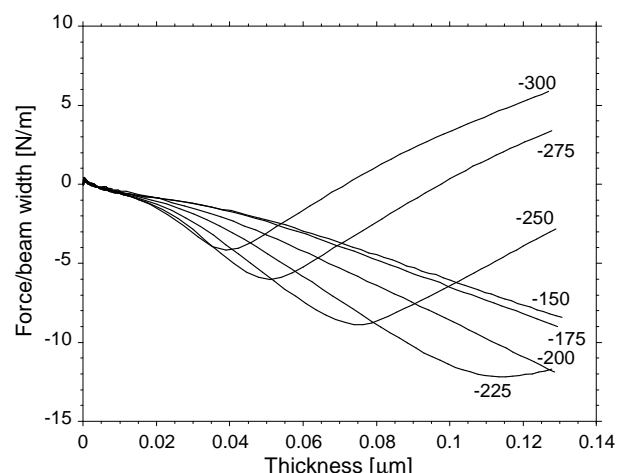

Figure 2. The force exerted on the cantilever beam electrode by the aluminum electrodeposit as a function of deposit thickness and deposition overpotential. Compressive stress in the film exerts a negative force while tensile stress exerts a positive force.

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