



Electroless atomic layer deposition of copper

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ABSTRACT

Electrochemical ALD enables the atomically-precise deposition of Cu films; however, in the traditional embodiment of electrochemical ALD, the underpotential deposition (UPD) step necessitates external electrode potential manipulation. This renders the process unsuitable for uniform deposition onto highly-resistive or electrically-isolated micro-patterned surfaces. To address this deficiency, we report herein the feasibility of electroless Cu ALD process consisting of: (i) Electroless UPD of a sacrificial Zn adlayer mediated by an organic reductant, followed by (ii) Spontaneous surface-limited redox replacement of the Zn adlayer by a Cu monolayer. These steps when repeated sequentially enable multilayered Cu films with minimal roughness.

1. Introduction

Atomically precise fabrication of materials is essential for future applications in nano-electronics. Over the last decade, electrochemical atomic layer deposition (e-ALD) has emerged as a low-cost, scalable means to achieve the requisite atomic-level control and precision needed in nano-scale film fabrication [1–5]. A recent embodiment of electrochemical ALD of Cu developed by the authors comprises of underpotential deposition (UPD) of a sacrificial adlayer of Zn followed by spontaneous replacement of the Zn_{upd} layer by a nobler Cu monolayer [5]. In conventional e-ALD processes, the UPD layer formation is performed potentiostatically, which implies that external control of the electrode potential is necessary. The need for external potential manipulation presents a drawback for many applications. Practically relevant substrates to be metallized in semiconductor devices are often highly resistive or contain micro-patterned geometries. The precise and uniform application of a predetermined electrode potential to all electro-active regions of a resistive or micro-patterned substrate is very challenging and often impractical. Therefore, the development of UPD processes in which external control of the substrate potential is not required is of great interest. Such a “contact-less” process would enable electroless versions of atomic layer deposition. To our knowledge, two such electroless processes have been reported in literature [6,7]. Cappillino et al. [6] reported atomic-layer electroless deposition by hydrogen (H) assisted modification of a palladium (Pd) electrode followed by substitution of the surface PdH layer by a nobler metal. Ambrozik et al. [7,8] reported an electroless approach in which Pb_{upd} formation was facilitated by the use of an “executive” Pb counter electrode rather

than direct electrode potential manipulation; however, this process still requires an external electrical contact during the UPD step. In the present work, we report on the electroless deposition of a Zn_{upd} adlayer facilitated through the use of glyoxylic acid reductant. Surface-limited redox replacement (SLRR) of Zn_{upd} by nobler Cu then enables atomic layer deposition in an electroless mode.

2. Experimental

2.1. Polarization studies

Linear sweep voltammetry (LSV) was utilized for studying glyoxylic acid (GA) oxidation on a PVD-Cu substrate with 1 cm² surface area. GA oxidation studies were performed in a three-electrode cell in which the Cu substrate served as working electrode, a platinum (Pt) wire served as counter electrode, and a saturated Ag|AgCl (Radiometer Analytical) electrode served as reference electrode. All solutions were prepared using analytical-grade chemical reagents and de-oxygenated DI water. The alkaline electrolyte (pH = 13 adjusted using KOH) for GA oxidation studies consisted of 190 mM glyoxylic acid monohydrate (CHOCOOH·H₂O, Acros Organics) at 60 °C (referred to as “GA only” electrolyte). The electrolyte was deoxygenated by bubbling argon (Ar) gas for 1 h prior to experiments. The electrode potential was scanned at 20 mV/s using PAR VersaSTAT 4 potentiostat. GA oxidation polarization was also investigated on a PVD-Cu substrate coated with a thin (~0.5 μm) layer of electroplated Zn.

Zn underpotential deposition (Zn_{upd}) studies were performed on a PVD-Cu substrate. The electrolyte employed for Zn_{upd} studies consisted

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of 1 mM zinc oxide (ZnO, Fisher Scientific) in pH = 13 solution (referred to below as “Zn only” electrolyte). Electrolyte temperature was 60 °C.

2.2. Two-compartment cell for Zn_{upd} studies

A two-compartment galvanic electrochemical cell was employed to demonstrate Zn_{upd} . One compartment contained “GA only” electrolyte whereas the other compartment contained “Zn only” electrolyte. The two compartments were connected by a porous frit. A PVD-Cu electrode (1 cm² surface area) was placed in each compartment. To facilitate spontaneous Zn_{upd} , the two Cu electrodes were contacted externally. Following Zn_{upd} on Cu, GA oxidation polarization measurements were performed on the same electrode but in a separate three-electrode cell using “GA only” electrolyte. Potential was scanned at 20 mV/s. These studies validated the presence of a Zn adlayer on Cu as discussed below.

2.3. Electroless ALD of Cu

A specialized substrate consisting of ruthenium (Ru) coated with a Cu_{upd} monolayer (ML) was used for demonstrating electroless Cu ALD. Conditions under which the Cu_{upd} ML can be formed are described elsewhere [9]. The use of Ru as substrate herein allows stripping coulometry characterization of the Cu deposited onto it. The Cu_{upd} ML minimizes substrate effects; however, in practical applications of electroless Cu ALD, the Cu_{upd} layer may not be required depending on the nature of the substrate surface. After Cu_{upd} ML deposition, the Ru substrate was dried under a stream of nitrogen, and then immediately immersed in an electrolyte containing 190 mM GA and 1 mM ZnO adjusted to pH = 13 and maintained at 60 °C (referred to as “complete electroless” electrolyte). This facilitated, under open-circuit conditions, spontaneous oxidation of GA which provided electrons for the reduction of $[Zn(OH)_4]^{2-}$ ions to a Zn_{upd} layer. After immersion in the “complete electroless” solution for 300 s, the substrate was removed and dried again. Then, it was immersed in an acidified (pH = 4) 100 mM $CuSO_4$ solution for 30 s to facilitate the spontaneous surface-limited redox replacement of electroless-deposited Zn_{upd} by a Cu ML. In some experiments, the electroless Zn_{upd} and SLRR process steps were repeated so as to deposit additional Cu MLs. During sample transfer between electrolytes, the substrate was rinsed in de-oxygenated DI water and dried under nitrogen gas. After electroless Cu ALD was complete, anodic stripping coulometry was performed to quantify the deposited Cu mass. The electrolyte employed for stripping coulometry consisted of 50 mM H_2SO_4 . During stripping, the potential was scanned from OCP to 0.4 V vs. Ag|AgCl followed by a potentiostatic hold at 0.4 V to completely strip the deposited Cu. The stripping charge density provided via Faraday’s law the mass density of Cu deposited during electroless ALD. Roughness of the electroless ALD Cu films was characterized using AFM.

3. Results and discussion

3.1. Polarization studies of GA oxidation and Zn_{upd}

Glyoxylic acid (GA) is widely used as a reducing agent in the bulk electroless deposition of Cu [10]; however, its use as reductant in adlayer formation by UPD has not been attempted. In this work, we studied GA oxidation on Cu using the “GA only” electrolyte (composition reported in experimental section) at pH = 13 and at 60 °C. Zn_{upd} formation was also investigated under similar conditions but from a “Zn only” electrolyte. Fig. 1 illustrates the polarization behaviors of the GA oxidation and the Zn_{upd} formation reactions. From Fig. 1, it is observed that at a potential of about –0.99 V vs. Ag|AgCl both GA oxidation on Cu and Zn_{upd} formation reactions are facilitated at equal rates (27 μA /

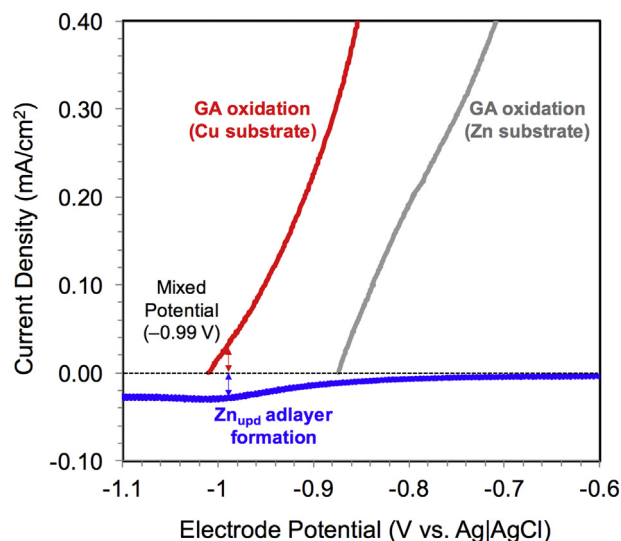


Fig. 1. Linear scan voltammograms showing the polarization behavior of (i) GA oxidation on Cu (red); (ii) GA oxidation on Zn (grey); and (iii) Zn_{upd} on Cu (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cm²). Thus, in accordance with mixed potential theory, GA oxidation can spontaneously induce Zn_{upd} formation at –0.99 V. Note that bulk electrodeposition of Zn occurs at potentials negative with respect to –1.5 V vs. Ag|AgCl when using $[Zn(OH)_4]^{2-} = 1$ mM. Also, at –0.99 V, H_2 co-evolution is minimal because of the alkaline medium and the high overpotential for HER on Zn [5]. Thus, the reductive current measured in the “Zn only” electrolyte (Fig. 1, blue curve) at –0.99 V corresponds to Zn_{upd} . From above observations, we conclude that GA oxidation can spontaneously trigger Zn_{upd} formation on Cu.

GA oxidation polarization was also investigated on a PVD-Cu substrate coated with a thin (~0.5 μm) layer of electroplated Zn. A substantial anodic shift in the GA oxidation polarization curve on Zn (compared to that on Cu) is evident in Fig. 1. This suggests that if a Cu substrate is completely covered with Zn, the GA oxidation reaction is rendered unfavorable. This property allows for self-terminating attributes of the electroless Zn_{upd} process as shown below.

3.2. Zn_{upd} in a galvanic two-compartment cell

The two-compartment electrochemical setup and protocol employed is depicted in Fig. 2 and details are discussed in experimental section above. In the absence of external contact between the Cu electrodes, one placed each in the “GA only” and the “Zn only” electrolytes, no Zn_{upd} adlayer is formed. This is confirmed via polarization measurements on the Cu electrode originally placed in the “Zn only” electrolyte and then transferred to a “GA only” electrolyte for characterizing the GA oxidation kinetics. The GA oxidation polarization behavior [shown in Fig. 2(a) in blue] closely matches that of GA oxidation on a blank Cu electrode [Fig. 2(a) in red] suggesting that Zn_{upd} formation was not facilitated in the two-compartment setup in the absence of external contact. In the presence of external contact, GA oxidation is facilitated on the Cu electrode in the left-side “GA only” compartment. This releases electrons which are transferred externally to the Cu electrode in the right-side “Zn only” electrolyte thereby facilitating Zn_{upd} . This is confirmed by polarization of the Zn_{upd} -covered Cu electrode in a “GA only” electrolyte. The GA oxidation now closely matches that on an electroplated Zn surface [Fig. 2(b)], which confirms presence of Zn_{upd} .

In the presence of an external electrical connection in the two-compartment cell, the GA oxidation reaction (left-side compartment) is:

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