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Cu and Cu(Mn) films deposited layer-by-layer via surface-limited redox replacement and underpotential deposition

J.S. Fang[a,*], S.L. Sun[a], Y.L. Cheng[b], G.S. Chen[c], T.S. Chin[c]

[a] Department of Materials Science and Engineering, National Formosa University, Huwei 63201, Taiwan
[b] Department of Electrical Engineering, National Chi-Nan University, Nan-Tou 54561, Taiwan
[c] Department of Materials Science and Engineering, Feng Chia University, Taichung 40724, Taiwan

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ABSTRACT

The present paper reports Cu and Cu(Mn) films prepared layer-by-layer using an electrochemical atomic layer deposition (ECALD) method. The structure and properties of the films were investigated to elucidate their suitability as Cu interconnects for microelectronics. Previous studies have used primarily a vacuum-based atomic layer deposition to form a Cu metallized film. Herein, an entirely wet chemical process was used to fabricate a Cu film using the ECALD process by combining underpotential deposition (UPD) and surface-limited redox replacement (SLRR). The experimental results indicated that an inadequate UPD of Pb affected the subsequent SLRR of Cu and lead to the formation of $PbSO_4$. A mechanism is proposed to explain the results. Layer-by-layer deposition of Cu(Mn) films was successfully performed by alternating the deposition cycle-ratios of SLRR-Cu and UPD-Mn. The proposed self-limiting growth method offers a layer-by-layer wet chemistry-based deposition capability for fabricating Cu interconnects.

1. Introduction

Layer-by-layer deposition of Cu films has been suggested as a technique with a microelectronics application potential for depositing a film with gap-filling capability [1]. There is a significant need in this deposition technique because higher aspect-ratio trenches/holes make gap-filling capability more challenging when the device sizes are continuously scaled down. Currently, a vacuum-based advanced sputter process is used for depositing a thin layer barrier to avoid Cu and Si intermixing followed by a sputtered Cu seed layer [1]. Then, a bulk Cu film is deposited using electrochemical deposition. The approach includes a vacuum process and a wet chemical process. Thus, it is not easy to use this approach in an in-line manner. Furthermore, gap-filling is problematic when feature sizes reduce to few tens of nanometer. Recent developments show that vacuum-based atomic layer deposition is capable of forming a superfilling film. In this study, we use an electrochemical variety of atomic layer deposition (electrochemical atomic layer deposition, ECALD) methodology that can fabricate microelectronics Cu interconnection using only wet processing. ECALD has been frequently used to prepare superlattice such as CdTe [2], HgSe [3], PbSe/PbTe [4], and Cd-ZnSSe [5]. Additionally, the method has been used to deposit Cu [6,7] and Ru [8] nanofilms. Furthermore, our previous results show that the copper-silver alloy film can be deposited using ECALD by controlling the deposition sequences of copper and silver [9].

Typical Cu interconnects require a metallic TaN/Ta barrier layer to prevent Cu diffusion to the interlevel dielectric and as an adhesion layer to the copper seed layer [10,11]. In general, the barrier layer has high electrical resistivity. This suggests that the use of Cu alloy film free from the barrier layer is promising for reducing the overall electrical resistivity of Cu-metallized films. Cu alloy films doped with a soluble or an insoluble metallic element can retard the detrimental reactions between Cu and Si and further improve the resistance to electromigration [12]. Specifically, during the forming-gas annealing, the doped Mn readily segregates to the interface, and forms a Mn-O passivation layer that prevents Cu diffusion [13–21]. Cu(Mn) films are most promising for interconnects in microelectronics. However, the addition of Mn to Cu affects the electrical resistivity because the resistivity of Cu(Mn) film increases with an increasing concentration of Mn [12]. Although comprehensive studies on Cu(Mn) films prepared via sputtering process have been previously reported [13–21], the sputtering process makes the film deposition with a high trench/hole aspect-ratio difficult.

Conventionally, Cu thin-film interconnects that are used in microelectronics are deposited using electrodeposition from a

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* Corresponding author.
E-mail address: jsfang@nfu.edu.tw (J.S. Fang).

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sulfuric acid electrolyte [22,23]. Mn is known to have a low redox potential in aqueous solutions (E^0 (Mn^{2+}/Mn) = − 1.18 V_{SHE}). Thus, its electrodeposition in an aqueous solution is difficult. However, recent studies have overcome the drawback. For example, co-deposition of Mn–Cu alloys has been performed on steel [24–26], which indicates that the alloy film can be deposited by selecting an appropriate deposition current density and the solution pH.

Previous studies have focused on the passivation behavior of steel by Mn–Cu films that contained high Mn concentration of approximately 97 at.% [24–26]. In this study, thin films of Cu and Cu(Mn) were deposited using ECALD. The Cu(Mn) films were deposited using underpotential deposition (UPD) and surface-limited redox replacement (SLRR). The UPD involves the deposition of one monolayer of one element on top of a second layer of another element at a potential slightly smaller than what is needed to deposit the element itself. The Cu^{2+} electrolyte in this study was introduced to replace the UPD-deposited Pb sacrificial material on the surface at an open circuit potential (OCP) due to the difference in the redox potential. UPD performs the deposition in less than one monolayer. Thus, the repetitive steps result in a layer-by-layer growth. The growth mechanism and the electrical properties of the resulting Cu and Cu(Mn) films will be discussed.

2. Experimental procedures

Cu and Cu(Mn) films were prepared using ECALD on Si(100) substrates that were coated with 10 nm of Ru. Prior to the electrochemical deposition process, the Ru/Si substrates were cleaned to remove any oxide layers. This was achieved using cyclic voltammetry at a scan rate of 10 mV/s in a 10 mM $HClO_4$ by scanning from +700 mV to −500 mV for 5 cycles.

To study the electrochemical deposition of Cu films, the first Cu monolayer was deposited on the substrate using UPD, followed by the sacrificial Pb layer deposition using UPD. Then, the next Cu monolayer was prepared by replacing UPD-Pb using SLRR. The cycle was repeated 50 times. The Cu electrolyte consisted of 1.0 mM $CuSO_4{\cdot}5H_2O$ (Hayashi Pure) and 4.0 mM H_2SO_4 (Shimakyu's Pure). The electrolyte for Pb deposition, which is a mixture of 1.0 mM $Pb(ClO_4){\cdot}2H_2O$ (Sigma-Aldrich) and 4.0 mM $HClO_4$ (Sigma–Aldrich), was introduced into the electrochemical cell, and the Pb-UPD was performed for 60 s. Next, the samples that were coated with the resulting sacrificial underpotential-deposited Pb layer were immersed into the Cu electrolyte, and the UPD-Pb was replaced by Cu at an open circuit potential for 60 s. A blank solution, 4.0 mM $HClO_4$ (Sigma–Aldrich), was used to remove the previous solution from the cell for 10 s. Pb^{2+} electrolyte is known to affect biological systems and cause environmental issues. Therefore, its application and waste disposal should require special attention following regulatory procedures.

For the Cu(Mn) film, the electrolyte used for Cu deposition consisted of 1.0 mM $CuSO_4{\cdot}5H_2O$ (Hayashi Pure) and 4.0 mM H_2SO_4 (Shimakyu's Pure). The electrolyte used for Mn deposition consisted of 1.0 mM $MnSO_4{\cdot}H_2O$ (Hayashi Pure) with 4.0 mM H_2SO_4 (Shimakyu's Pure) and 0.75 mM $(NH_4)_2SO_4$ (Hayashi Pure). All solutions were at pH 3.5 and were adjusted using NaOH (J.T. Baker) for the Cu and Pb solutions and using NH_4OH (Hayashi Pure) for the Mn solution. The Cu(Mn) films were prepared layer-by-layer by alternating SLRR-Cu and UPD-Mn for a total of 50 cycles. This resulted in the final thickness of ~10.0 nm. The auxiliary electrode was a gold wire that was attached on the cell wall opposite from the substrate. The reference electrode was Ag/AgCl (3 M NaCl, Bioanalytical Systems Inc.). Annealing of the Cu and Cu(Mn) films was performed in a rapid thermal annealer (RTA) at the temperature from 200 °C to 600 °C for 5 min under argon protection.

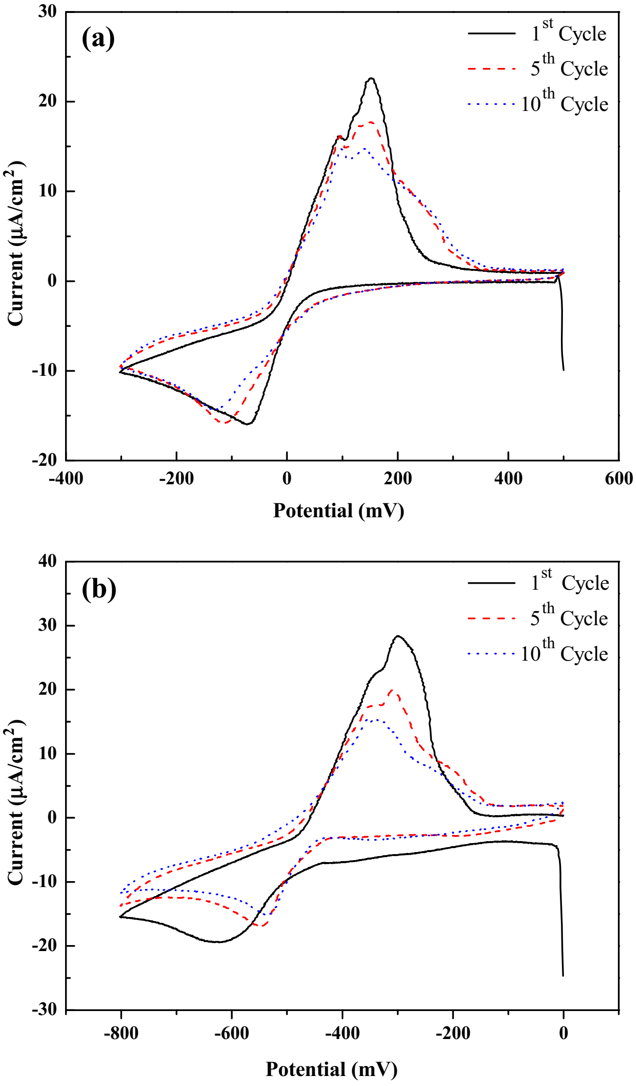

Fig. 1. (a) Cyclic Voltammetry scans of Cu on a Ru/Si (b) Pb on a Cu/Ru/Si at a scan rate of 10 mV/s.

X-ray diffractometry (XRD, MacScience M03XHF22) with Cu-$K_{\alpha1}$ radiation was performed to investigate the crystal structure. A standard four-point probe electrical resistivity measurement was conducted on the film surface to determine the electrical resistivity. X-ray photoelectron spectroscopy (XPS), excited by Mg-K_α radiation (1253.6 eV) operated at 15 kV, was performed using a PHI 1600 system to obtain the detailed photoelectron spectra. The binding energies were calibrated using C1s peak at 284.6 eV as a reference.

3. Results and discussion

3.1. Properties of SLRR-Cu films using a sacrificial UPD-Pb

Prior to layer-by-layer deposition of Cu, cyclic voltammetry (CV) was performed to determine the UPD of Cu and Pb. Fig. 1a presents the CV scans of Cu^{2+} electrolyte on a Ru/Si substrate from +500 mV to −300 mV at a scan rate of 10 mV/s because the Cu reductive potential and the oxidation potential of Cu on Ru electrode are within the scan range [6,9,27,28]. Decrease in current density begins at +100 mV during the down scan in the positive potential region and a peak occurs at −73 mV during the first scanning cycle. Subsequent CV scans show a reductive feature at a more negative potential. This occurs due to the decrease in ion concentration in