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Atomic layer deposition of copper and copper silver films using an electrochemical process

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ABSTRACT

This paper describes the formation and properties of Cu and Cu(Ag) films on a Ru/Si substrate using electrochemical atomic layer deposition. The process was performed layer-by-layer using underpotential deposition (UPD) and surface-limited redox reactions. The first Cu atomic layer was deposited on the Ru/Si substrate via UPD. Using UPD, atomic layered of Pb, which acts as a sacrificial layer, was applied on the Cu layer. Then, a Cu^{2+} solution was flushed into the cell at an open-circuit potential, and the Pb layer was exchanged for Cu via redox replacements. The above sequences were repeated 500 times to form a Cu film. The Cu(Ag) alloy films were formed using Cu–UPD and Ag–UPD in predetermined sequences. The lowest electrical resistivity achieved was 3.6 and 2.2 μΩ cm for the Cu film and Cu(Ag) film, respectively, after annealing at 400 °C. Due to the self-limiting reactions, the process has the ability to deposit atomic layers to meet the requirement of Cu interconnects.

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1. Introduction

Copper has been used as interconnects in ultra large scale integrated circuits (ULSI) because Cu has a high electrical conductivity and high resistance to electromigration. Typical Cu interconnection requires a barrier to prevent Cu diffusion because detrimental reactions occur between Cu and silicon (Si) at a temperature as low as 200 °C [1,2]. The barrier layer typically has a high electrical resistivity, which suggests the use of Cu alloy film free from the barrier. Cu-alloy films, which dope Cu with soluble or insoluble elements, can retard the intermixing between Cu and Si and further improve resistance to electromigration.

As the feature sizes used in the ULSI decrease toward 16 nm, a process that deposits a conformal Cu film is urgently needed. Many researchers have extensively studied Cu and Cu-alloy films prepared by sputtering [3–5]. However, a damascene process is used to produce copper interconnections during the manufacturing of ULSI. A wet electrochemical process is employed to deposit the Cu film. Therefore, an electrochemical method to prepare high quality Cu films is essential for ULSI at technology nodes that are a few tens of nanometers in size. Currently, atomic layer deposition (ALD) is typically employed because it is capable of forming a conformal film to deposit these layers, especially for deep trenches and vias. In this study, the electrochemical form of ALD (electrochemical atomic layer deposition, ECALD) enables for the formation of Cu interconnection to be an entirely wet process [6–8].

To maintain the lowest possible electrical resistivity of the Cu alloy film, a Cu(Ag) film may be a potential material for interconnects in microelectronics. In this study, Cu and Cu(Ag) were deposited on Ru/Si substrates using ECALD. According to the fabrication of copper interconnects in microelectronics, electroplating was employed to deposit the Cu(Ag) alloy films from a sulfuric acid electrolyte [9,10]. The underpotential co-deposition of Au–Cu alloys has been performed [11], indicating that the copper alloy film can be co-deposited by selecting the appropriate deposition potential of a mixing solution. By adjusting the concentration of the solution, precise alloy composition control using underpotential deposition (UPD) can be achieved. Cu(Ag) deposition using UPD by ECALD is reported for the first time. The UPD involves the deposition of an atomic layer of one element on a second layer of an element at a potential prior to that needed to deposit the element on itself. The process of layer-by-layer atomic deposition and the electrical properties of the resulting Cu and Cu(Ag) films will be discussed.

2. Experimental details

The substrate for the electrochemical deposition of Cu and Cu(Ag) films was Si (100) coated with 10 nm Ru. The Ru layer was deposited by direct current sputtering at a power of 100 W. The base pressure of the vacuum chamber was 2.0×10^{-6} Torr, and the working pressure was 4.0×10^{-3} Torr during sputtering under a constant argon flow rate of 20 sccm. No intentional heating or cooling of the substrate was performed during Ru sputtering. Prior to the electrochemical process,

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the Ru/Si substrate was cleaned to remove any possible oxide layers by cyclic voltammetry in 10 mM $HClO_4$ at a scan rate of 5 mV/s.

To study the electrochemical deposition of Cu film, the first Cu monolayer was performed by UPD, and then, a layer of Pb was applied by UPD for use as a sacrificial metal. Finally, the next Cu monolayer was prepared by replacing Pb using a surface limited redox reaction (SLRR), and this cycle was repeated 500 times. The Cu solution consisted of 1 mM $Cu(ClO_4)_2 5H_2O$ (Sigma-Aldrich), 2.5 mM HCl (Sigma-Aldrich), and a range of NaCl concentrations from 10 mM to 70 mM. The electrolyte for the Pb deposition, which consisted of 1 mM $Pb(ClO_4)_2H_2O$ (Sigma-Aldrich) + 2.5 mM HCl (Sigma-Aldrich), was introduced into the electrochemical cell, and the UPD was performed for 60 s. Next the resulting sacrificial deposited Pb layer was immersed into the Cu electrolyte, and the Pb was replaced by Cu at an open circuit potential (OCP) for 60 s. 10 mM $HClO_4$ (Sigma-Aldrich) was used as a blank solution to remove the previous solution from the cell for 10 s. For the Cu(Ag) multilayers, the electrolyte use for Cu deposition consisted of 1 mM $Cu(ClO_4)_2 5H_2O$ (Sigma-Aldrich) with 2.5 mM HCl (Sigma-Aldrich), and the electrolyte used for Ag deposition consisted of 10 mM $AgNO_3$ (Mallinckrodt) with 5 mM H_2SO_4 (Samakyu's Pure Chemical). The Cu(Ag) multilayers were prepared layer-by-layer by alternating UPD–Cu and UPD–Ag. All of the solutions were prepared using deionized water. The solution was deaerated by bubbling with high purity nitrogen for 1 h prior to deposition. The auxiliary electrode consisted of a gold wire embedded on the cell wall opposite to the substrate. The reference electrode was Ag/AgCl (3 M NaCl, Bioanalytical Systems Inc.). Anodic stripping of the deposited Cu film was performed in the blank solution (i.e., 0.5 mM H_2SO_4) to estimate the total Cu coverage in monolayers (MLs) per deposition cycle. A post-annealing treatment was performed on the as-deposited Cu and Cu(Ag) films at 400 °C for 5 min under argon protection.

X-ray diffraction (XRD, MacScience M03XHF22) with $CuK_{\alpha1}$ radiation was used to investigate the crystal structure. The electrical resistivity was measured using a standard four-point probe apparatus at room temperature.

3. Results and discussion

3.1. Surface limited redox reaction deposition of Cu on the Ru/Si substrate

Electrochemical atomic layer deposition of Cu on a Ru metallized Si substrate is important because Ru is promising as a seed layer for Cu electrodeposition [12]. The electro-potential for the UPD of Cu on Ru/Si was determined using cyclic voltammetry (CV). Fig. 1 shows the first three CV scans from +500 mV to −800 mV at a scan rate of 5 mV/s. Copper was electroplated in a 1 mM $Cu(ClO_4)_2 5H_2O$ solution with 2.5 mM HCl and 40 mM NaCl. The freshly cleaned Ru/Si substrate was scanned starting from an OCP value of +500 mV down to a negative maximum of −800 mV. Copper deposition begins at +90 mV during the down scan in the positive potential region and peaks at −15 mV and −50 mV. During the reverse scan (up scan from −800 mV to 500 mV), Cu stripping begins at −50 mV and peaks at +130 mV and +180 mV.

UPD of Cu can be obtained at −50 mV, which is more negative than that reported for Cu on Au/Ti/glass-substrate (+300–+325 mV) [8], because UPD conditions vary in different electrolytes and substrates. This step is followed by the bulk deposition of Cu at a more negative potential. UPD implies that surface limited deposition should occur at potentials before the formal potential for bulk deposition of Cu. The reductive peak at −50 mV was chosen for depositing the first Cu atomic layer to achieve a high coverage of Cu atoms. The shoulder at −15 mV results from the electrolyte solution containing Cl^- ions. The Cl^- ions induced the deposition of Cu atoms in a Cu–Cl complex [13,14]. The oxidation peak at +130 mV corresponds to the oxidation of the Cu layer to deposition at a reductive potential of −50 mV. The oxidation peak at 180 mV is related to the reduction peak at −15 mV, and this peak is due to the dissociation of the Cu–Cl complex. Because the Cl^--induced structure had an ordered superstructure, its deposition and stripping are reversible [13–17].

The potential for the UPD of Pb on Cu/Ru/Si was also determined using a CV scan. Pb has a lower reduction potential. Therefore, the scan range is from 0 mV to −800 mV to avoid hydrogen generation. The first three CV scans are shown in Fig. 2. The CV scan cycle after a previous one occurs at a higher potential and experiences a different reductive feature. A sharp increase starts at −450 mV in the reductive current. In addition, a distinct reductive peak was observed at −575 mV for the first scan cycle. The redox peak current decreases with increasing CV cycles due to a decreased concentration of ions in the solution after previous scans. To avoid bulk deposition, a potential of −475 mV was chosen for the UPD of Pb. The UPD of Pb is significantly more negative than that of Cu because Pb has a lower work function than that of Cu. The positive going scan experiences two distinct oxidation peaks at −350 mV and −270 mV. The shape of the CVs is very sensitive to the surface nature of the electrode and exhibits a pronounced change in the anodic shape when after several CV scans. The shape difference of the CV scans confirms the atomic crystalline rearrangement of the surface Cu at −350 mV during Pb stripping, which corresponds to the bulk oxidation potential of Pb at −270 mV [18].

First, the UPD of the Cu film was executed at −50 mV for 60 s to deposit the first Cu layer. Next, the UPD of Pb was performed at

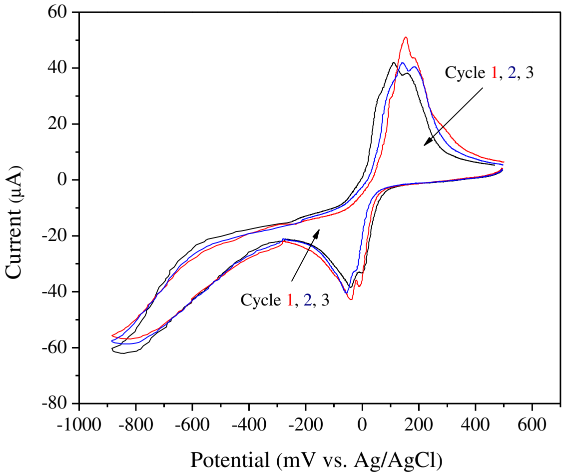

Fig. 1. CV scans of Cu on a Ru/Si using Cu-perchlorate solution with 40 mM NaCl at a scan rate of 5 mV/s.

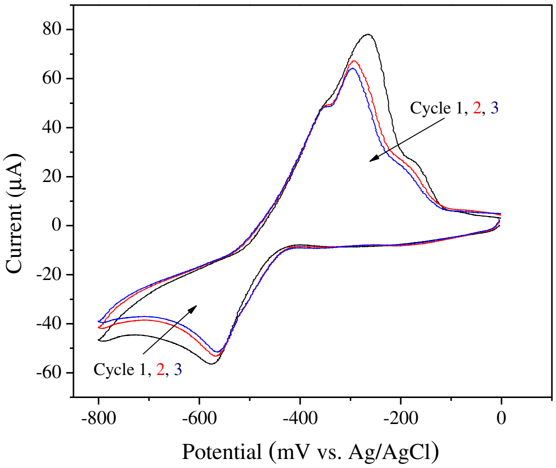

Fig. 2. CV scans of Pb on Cu/Ru/Si using a Pb-perchlorate solution with 40 mM NaCl at a scan rate 5 of mV/s.

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