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Effects of the substrate temperature on the Cu seed layer formed using atomic layer deposition

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ABSTRACT

Cu has replaced Al as the main interconnection material in ultra-large integrated circuits, reducing resistance capacitance delay and yielding higher electro-migration reliability. As feature size decreases, however, it has become more difficult to produce reliable Cu wiring. We studied a Cu seed layer deposited using plasma enhanced atomic layer deposition (PEALD). The electrical properties of the PEALD Cu thin film with sub-10 nm thickness were determined by the continuities and morphologies of the films. At a deposition temperature of 150 °C, the resistivity of Cu thin films was 5.2 μΩ-cm and the impurity content was below 5 atomic %. Based on these results, Cu seed layers were deposited on 32-nm Ta/SiO2 trench substrates, and electrochemical plating was performed under conventional conditions. A continuous seed layer was deposited using PEALD, resulting in a perfectly filling of the 32-nm sized trench.

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1. Introduction

Copper (Cu) is a suitable material for interconnects because of its low resistivity (1.67 μΩ-cm) and high electromigration resistance [1–3]. Currently, an electrochemical plating (ECP) process is used to fabricate Cu interconnects because a bottom-up mode, superfilling, can produce interconnects without voids or seams. A thin, continuous seed layer with low resistivity is necessary for ECP, and this seed layer strongly influences the characteristics of Cu interconnects, including conductivity, preferred orientation and density. If the Cu seed layer is discontinuous or too thick, or does not conform to the substrate, a void may remain after being filled by ECP [4]. Also, to perform an ECP, the seed layer should be thin and highly conductive. Currently, the most common method for depositing a seed layer is ionized physical vapor deposition (i-PVD), which increases the deposition rate along the side walls of a trench or hole by enhancing the properties of metal ions. To maintain decreased feature size and increased aspect ratio, a conformal seed layer with a thickness of several nm is required, and i-PVD techniques have reached their limits regarding these requirements. Electroless plating and atomic layer deposition (ALD) are being discussed as alternative methods for depositing seed layers [5,6]. However, Cu wires formed on electroless plated Cu seed layers have high resistivity due to the diffusion of Pd into the upper Cu wire, and, furthermore, precise control of thickness is difficult. ALD, on the other hand, is a suitable technique for forming seed layers because it produces thin films with high purity and uniformity and allows for precise thickness control [6,7]. ALD films have these properties because ALD is based on self-limiting surface reactions with a substrate. Plasma enhanced ALD (PEALD) can also reduce substrate temperature and allows for deposition of thin films with higher purity because plasma allows for effective decomposition of a precursor [8,9].

The increase in resistivity with decreasing metal thin film thickness is regarded to be driven by grain boundary and surface scattering [10,11]. In many studies about metal ALD, the resistivity of ALD metal thin films with thicknesses of several nm is either not reported or is so high that its magnitude must be due to either discontinuity or scattering factors. Although ALD characteristics were identified, films with thicknesses of several nm to dozens of nm were observed to be unlike oxide or nitride ALD films. Cu, a transition metal, has a relatively high surface energy, resulting in island mode growth as long as sufficient activation energy is available. Film deposition follows Young's equation (Eq. (1)) [12],

$$\cos\theta = \frac{\lambda_s - \lambda_i}{\lambda_c} \tag{1}$$

where θ is the wetting angle of the deposited film, λ_s and λ_c are the surface energies of the substrate and the deposited film, respectively, and λ_i is the interfacial energy between the film and the substrate. Although research of ALD metal thin films, including Cu, has recently been published [13], in contrast to reports related to oxides and

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nitrides, reports about the effects of the substrate temperature on the properties of metal thin films are rare. In this study, we investigated the effects of morphology, surface roughness, crystal structure, impurities and varying substrate temperatures on the electrical properties of Cu thin film and evaluated its potential for use in seed layers.

2. Experimental details

Bis(1-dimethylamino-2-methyl-2-butoxy)copper (MABOC) was selected as the copper precursor for these PEALD experiments. Under standard conditions, the precursor is a volatile purple liquid and can be stored in an inert gas atmosphere for months without decomposition. MAOBC allows reproducible feeding of the precursor based on its own vapor pressure without introducing a carrier gas. This is possible because the precursor has high vapor pressure (93 Pa at 70 °C) and does not contain fluorine, which deteriorates adhesion with the substrate. Also, for practical applications, no problems related to particle generation associated with the use of a solid precursor arose.

Tantalum deposited on a thermal oxide covering a Si plane and trench was used as the substrate. A plane substrate (Ta(10 nm)/SiO_2 (100 nm)/Si), i.e., without trenches, was used to analyze Cu thin film properties and a 32 nm sized trench substrate (Ta(3 nm)/SiO_2 (100 nm)/Si) was used to evaluate the performance of PEALD Cu thin films as seed layers. The feeding lines were heated to 85 °C to prevent condensation of the precursors. Both the H_2 and N_2 flow rates for the precursor purge were fixed at 100 sccm, and 50 sccm of Ar gas was introduced as a reactant purge pulse. The power of the radio frequency plasma was fixed at 200 W. One unit cycle consisted of a precursor feeding pulse, a precursor purge pulse, a reactant feeding pulse, and a reactant purge pulse. Measuring the growth rate of the PEALD Cu thin film while increasing the precursor feeding time and purge time up to 5 s and 10 s, respectively, confirmed the self-limiting ALD process. To check the PEALD window, Cu thin films were deposited at varying substrate temperatures from 100 to 350 °C. Cu super-filling in the trench substrate was performed by the ECP solution, which contains polyethylene glycol as a suppressor and a sulfopropyl sulfonate as an accelerator [14]. The composition of the Cu ECP solution and a summary of conditions are given in Table 1.

The film thicknesses and the microstructures of Cu seed layers deposited on the 32-nm trench substrate were analyzed using scanning transmission electron microscopy (STEM; Hitachi HD-2300A). Sheet resistance was measured with a four-point probe (JANDEL) and Hall measurement system (Ecopia HMS-3000). High-resolution X-ray diffraction (XRD; Rigaku D/max-2500/pc, Cu-Kα = 1.54062 nm, Japan) analysis was applied to study the crystallinity. The surface structure, morphology, and roughness of ALD Cu thin films were studied by field-emission scanning electron microscopy (FE-SEM; JES 6340F, JEOL; operating voltage = 10.00 kV) and atomic force microscopy (AFM; Seiko Instrument SPA-400) in tapping mode. The impurities of the thin films were measured by X-ray photoelectron spectroscopy (XPS; SIGMA PROBE, Thermo VG). The XPS data were acquired using MgKα X-rays (1253.6 eV). Prior to XPS measurement, pre-sputtering to eliminate surface oxidation layer of Cu films was performed with an Ar^+ ion gun operated with a beam voltage of 3 keV. The adhesion of the Cu thin films to the Ta diffusion barrier layer was examined with a tape-test using 3 M Scotch tape.

Table 1
Chemical composition of ECP Cu solution and working condition.

Cu electroplating solution	
$CuSO_4 \cdot 5H_2O$	0.26 M
H_2SO_4	2.00 M
HCl	50 ppm
PEG4000 (Suppressor, polyethylene glycol)	100 ppm
SPS (Accelerator, sulfopropyl sulfonate)	1000 ppm
Working condition	
Temperature	R. T.
Applied current	0.01 A/cm^2
Plating time	240 s

3. Results and discussion

Fig. 1 shows the dependence of the growth characteristics of Cu PEALD on precursor feeding time and precursor purge time. The MABOC precursor feeding time and the precursor purge time varied from 1 to 7 s, respectively, while the pulse time of H_2 plasma was fixed at 4 s. As shown in Fig. 1(a), a precursor feeding time of 5 s and a precursor purge time of 3 s were confirmed to be enough to complete the self-limiting reaction of the MABOC precursor. In order to check the PEALD window with respect to the substrate temperature, the growth rate of Cu thin films was measured between substrate temperatures of 100 and 220 °C, Fig. 1(b). Cu thin films deposited at substrate temperatures between 100 and 180 °C exhibited ideal self-limiting and complementary reactions, while substrate temperatures above 180 °C led to chemical vapor deposition growth. The growth rates of Cu thin films showed a linear relationship with deposition cycle, with a growth rate of about 0.65 Å/cycle.

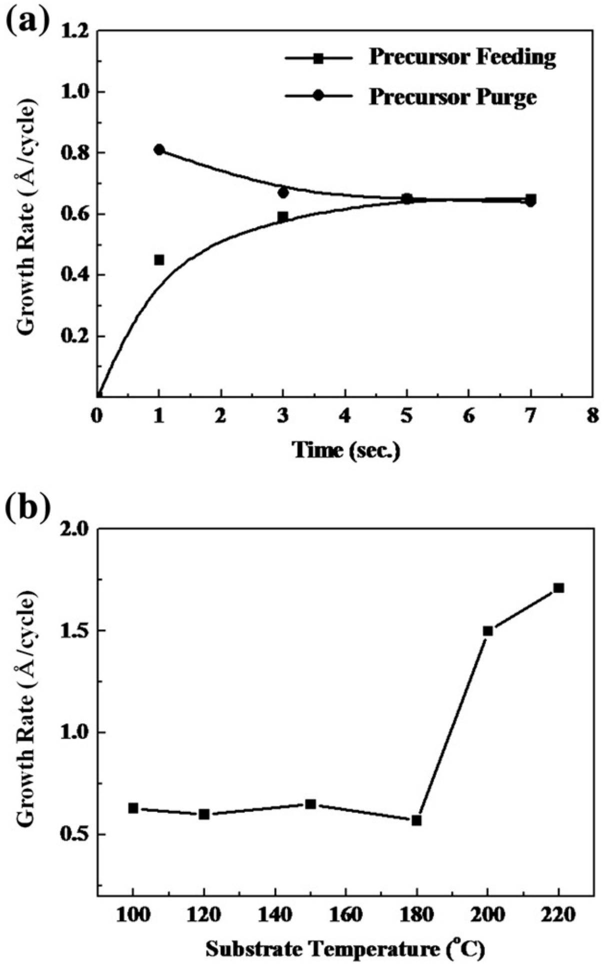

Fig. 1. The growth characteristics of PEALD Cu deposited on the SiO_2 substrate. (a) Growth rate of Cu thin films deposited using ALD as a function of Cu precursor feeding time and precursor purge time at a substrate temperature of 150 °C and (b) the growth rate of Cu thin films with a fixed feeding time of 5 s and a purge time of 3 s as a function of the substrate temperature.

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