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The influence of pulse plating frequency and duty cycle on the microstructure and stress state of electroplated copper films

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ABSTRACT

In this work, the impact of pulse electroplating parameters on the cross-sectional and surface microstructures of blanket copper films were studied using electron backscattering diffraction and x-ray diffraction. The films evaluated were highly (111) textured in the direction perpendicular to the film surface. The degree of preferential orientation was found to decrease with longer pulse on-times, due to strain energy density driven growth of other grain orientations. Residual biaxial stresses were also measured in the films and higher pulse frequencies during deposition led to smaller biaxial stresses in the films. Film stress was also found to correlate with the amount of twinning in the copper film cross-sections. This has been attributed to the twins' thermal stability and mechanical properties.

1. Introduction

Pulse electrochemical deposition (PED) is often used to deposit copper (Cu) interconnects and 3D structures for microelectronic applications due to its low cost and ability to deposit low defect density structures [1–3]. Highly textured and nanotwinned Cu interconnects are desirable for these applications as they may help reduce stresses caused by thermal fluctuations in 3D integrated circuits, increase their reliability, and electromigration resistance [4–7]. PED has been shown to enable more control over the deposition process than conventional direct circuit (DC) electroplating due to the tunable on- and off-times of the current pulse waves. During DC electroplating, a diffusion layer builds up around the cathode, impeding potential adatoms from reaching the surface of the electrode, thus slowing the growth rate and the mechanical properties of the deposits. The pulse off-time in PED serves to dissipate this blocking layer and distribute ions uniformly throughout the bath, allowing higher deposition efficiencies and uniformity [8–11].

Multiple prior studies in pulsed deposition have focused on peak current density (PCD) effects on resulting Cu microstructure. For example, smaller grains have been observed in Cu films with higher PCD, since the higher current densities result in faster nucleation rates from increased cathodic overpotential [12–15]. Increased bath temperature also gives rise to larger grain sizes in Cu films [14,15]. Furthermore, metal grain size and twinning have been found to be correlated in pulse electrodeposited copper films [12,16].

While in-situ deposition stress measurements have been conducted via wafer curvature techniques by D. Xu et al. [17–19], the resulting Cu microstructure has not been studied extensively with such PED pulse parameters as frequency and duty cycle. As shown in these studies and in the present effort, such deposition process variables can not only impact stress, but can also affect the extent of twinning in the deposited film, a desirable attribute. For example, bath additives and high stir rates can lead to the production of nanotwins in Cu [20,21]. Furthermore, increasing current density has been shown to create more densely packed nanotwins [22–24]. These nanotwinned Cu microstructures have high mechanical strength characteristics without sacrificing Cu's low electrical resistance [5,21,24]. Twin boundaries differ from grain boundaries since they do not adversely impact electron-mobility, yet they still hinder dislocation movement similar to that of high angle grain boundaries [5,25]. The spacing of these nanotwins has also been shown to dictate the strength of the material [5,7,24] and can be tuned with PCD [20,22]. PED is capable of producing nanotwins more readily than direct current ECD [20]. The pulse wave is thought to play an important role in the development of these

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twins. It is theorized that stresses accumulate during the on-times and relax out during the pulse off-times from recrystallization, creating twins [17–19].

Nanotwins are typically associated with (111) oriented Cu [20,22,26]. Since most Cu nanotwins are coherent, their boundaries are 60° rotations about the {111} plane. While (111) oriented Cu films can be achieved, it is far more common to see (110) oriented films, especially at larger thicknesses (>5 μm) [12,16,27]. Furthermore, peak current density has also been shown to affect film orientations [23]. Cu film texture is also dependent on the deposition substrate [22,28]. Stainless steel substrates produced more evenly distributed Cu grain orientations compared to MP35N alloy substrates which resulted in preferential {111} orientations at lower PCD and {110} orientations at higher PCD [22].

Hence, while the impact of pulse current densities on the microstructure in Cu films has been studied extensively, limited research has been carried out to directly correlate the employed pulse wave parameters to the resulting microstructural features in Cu films. This study specifically relates to the resulting cross-sectional microstructure and not only the film's surface morphology. The focus of this study is the examination of the effects of the PED's pulse frequency and duty cycle on the resulting Cu film's cross-sectional grain size, orientation, twinning, and stress state. Understanding and tuning of these attributes in blanket films is the first step towards fabricating advanced geometries, such as through silicon vias (TSV) [29]. Correlation of such process parameters with film attributes is required to enable improved reliability and electrical performance of Cu in microelectronics [30].

2. Experimental procedure

2.1. Pulsed electrochemical deposition of Cu films

Pulsed electrochemical deposition (PED) was conducted using a galvanostatic two electrode setup with a Puratronic 25 × 25 × 2 mm 99.999% pure Cu foil as the anode. Copper (Cu) films were deposited onto PED-ready silicon wafers (SKW Associates, Santa Clara, CA).[1] Test substrates were comprised of unpatterned 550 nm tetraethylorthosilicate (TEOS) isolation liner, 25 nm tantalum (Ta) barrier layer, and a 100 nm Cu seed layer (shown schematically in Fig. 1). PED was performed with an acid-based electrolyte bath, containing 200 g/L of $CuSO_4 \cdot 5H_2O$, 50 g/L of ACS grade H_2SO_4, and 50 mg/L of ACS grade HCl. The bath was degassed at ~7000 Pa with Air Liquide's 99.999% ultra-high purity nitrogen for 30 min prior to deposition. Depositions were conducted at room temperature under ambient conditions at stirring rates of 200 rpm. After deposition, the films were annealed at 150 °C for 1 h under forming gas (4% H_2/96% N_2) atmosphere to stabilize the microstructure and hinder uncontrolled room temperature recrystallization.

Nine deposition conditions were investigated in this study to evaluate the process parameter windows of interest (Table 1). The initial deposition conditions of 80 mA/cm^2 peak current density, 0.1 s on-time, and 0.5 s off-time were based off findings from Hsiao et al., who reported a high degree of nanotwins and texture in electroplated Cu at these conditions [20]. The frequency and duty cycle were varied from this base parameter set. Three samples were deposited per condition, with a target thickness of 3000 ± 300 nm. These thicknesses were evaluated using a Zygo NewView 8300 white light interferometer. For the higher degree of accuracy required for stress measurements, Rutherford Backscattering Diffraction (RBS) and focused ion beam (FIB) cross-sectional thickness measurements were conducted. All three thickness measurement techniques produced similar results and FIB thickness measurements were used for stress approximations.

[1] Certain commercial equipment, instruments, or materials are identified in this paper to specify experimental or theoretical procedures. Such identification does not imply recommendation by NIST nor the authors, nor does it imply that the equipment or materials are necessarily the best available for the intended purpose.

Fig. 1. A cross-sectional illustration of the substrate before copper electroplating.

2.2. Microstructural evaluation: EBSD and XRD

The cross-sectional microstructure of the films was evaluated via electron backscattering diffraction (EBSD) on the Hitachi SU-6600 scanning electron microscope (SEM) at Clemson University's Electron Microscopy Laboratory (United States). To obtain the surface quality necessary for electron backscattering diffraction (EBSD), a sample preparation procedure was used from previous studies [30]. The sample's cross sections were first polished with diamond lapping paper and finished with a 0.05 μm alumina slurry, followed by FIB milling using the Hitachi NB5000 dual beam SEM/FIB. Inverse pole figures and maps from the EBSD were examined to measure grain sizes, orientations, and twin characteristics of the film cross-sections.

X-ray diffraction (XRD) was performed on the films with the PANalytical XPert3 MRD XRD at the University of Central Florida's Materials Characterization Facility to confirm the texture results provided by EBSD. The XRD used a 1.5406 Å Cu K-alpha source to measure from 35° to 95° 2θ with a step size of 0.01 and 0.5 s per step. The texture coefficients (TC) of the four major Cu peaks, (111), (200), (220), and (311), were calculated from the diffraction pattern using the following equation:

$$TC = \frac{I_{hkl}/I^0_{hkl}}{(1/n)\sum I_{hkl}/I^0_{hkl}} \quad (1)$$

where I_{hkl} is the intensity of the hkl peak of interest, I^0_{hkl} is the peak intensity of randomly oriented Cu, and n is the number of peaks in the diffraction pattern. Fig. 2 shows a typical XRD diffraction pattern for a Cu film used in this study.

2.3. Residual stress measurements

Biaxial stress ($\boldsymbol{\sigma}$) was approximated through the Stoney formula [31] by measuring the radius of curvature of the substrate before and after deposition. The Stoney formula assumes the thickness of the substrate is much larger than that of the film and measures the added stress from its equilibrium state (before deposition). The radius of curvature was obtained through surface mapping with the Zygo NewView 8300

Table 1
The deposition pulse parameters used in this study.

PED condition #	Pulse signature			
	On-time [ms]	Off-time [ms]	Frequency [Hz]	Duty cycle
1	50	950	1	0.05
2	100	900	1	0.1
3	250	750	1	0.25
4	1	19	50	0.05
5	2	18	50	0.1
6	5	15	50	0.25
7	0.5	9.5	100	0.05
8	1	9	100	0.1
9	2.5	7.5	100	0.25