



Prediction of recrystallization times in electroplated copper thin films



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ABSTRACT

Room temperature recrystallization responses of blanket electroplated Cu thin films deposited under various conditions were monitored in real-time using synchrotron X-ray diffraction. Nominal control of electroplating parameters such as plating current, bath chemistry, and plating time was found to be insufficient to ensure repeatability of the 50% recrystallization time, τ_{50} , from sample to sample even though the thickness variations between samples were insignificant. Real-time X-ray analysis of samples from numerous electroplating baths showed that, for a given seed deposition process, a reliable estimation of τ_{50} at room temperature can be obtained from the ratio of the integrated intensities of the 111 and 200 Cu reflections, $\bar{I}_{111} / \bar{I}_{200}$, of the electroplated film at time zero (immediately after plating). Among the plating parameters investigated seed-layer texture most influenced this ratio and, hence, the subsequent room temperature recrystallization behavior of the plated film.

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1. Introduction

Freshly electroplated copper thin films can undergo large microstructural changes at room temperature. Despite several decades of research there is no consensus on the energetics and kinetics associated with these changes [1]. Part of the problem is due to the lack of repeatability between electroplated samples. Typically, ensuring repeatability in electroplating is approached through imposing tight controls on plating current, time, and chemistry [2–12]. However films plated under nominally identical conditions can show different recrystallization responses; samples obtained from different areas of a single wafer can also show differences in recrystallization times [4,7]. These effects are usually ascribed to thickness variations. To obtain a better metric of sample repeatability we used real-time synchrotron X-ray diffraction [3,13] to study microstructural changes from electroplated films deposited with a variety of frequently employed, phenomenological plating parameters. These included plating time and film thickness [4,13], seed layer deposition methodology [5,6], seed layer and plated film

texture [7,8], diffusion barrier chemistry [9,10], and impurity concentration [11,12].

Our results, summarized in Fig. 1, showed that 50% recrystallization times (τ_{50}) were strongly correlated with the ratio of the integrated intensities of the 111 and 200 Cu reflections, $R_{Tx} = \bar{I}_{111} / \bar{I}_{200}$, of the electroplated film at time zero, ($\tau = \tau_0$). This observation agrees with the findings by Ueno et al. [7] who reported results from a much smaller sample set (three samples). In addition we observe the presence of a critical initial texture ratio, R_{Tx}^* , which separates two regions where the dependency of τ_{50} on R_{Tx} is opposite. For $R_{Tx} > R_{Tx}^*$, τ_{50} increases with increasing R_{Tx} . For $R_{Tx} < R_{Tx}^*$, the opposite trend is observed. Over each range R_{Tx} can be used to predict τ_{50} , independent of the film thickness and other process parameters. Thus, this ratio can be utilized as a reliable metric for the a priori estimation of the recrystallization times of electroplated blanket Cu thin films, unlike prior studies [11,14,15], which were based on impurity or plating chemistry dependent indicators.

2. Analysis technique

X-ray diffraction experiments record the intensity of elastically scattered X-ray photons by a crystalline sample as a function of scattering angle, 2θ . For a polycrystalline thin film the measured intensity is the

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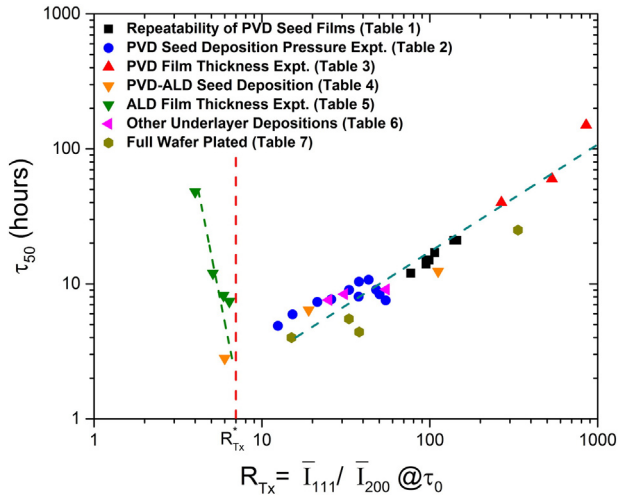


Fig. 1. Initial $\bar{I}_{111}/\bar{I}_{200}$ ratio for all Cu films used in this study presented as a function of recrystallization time, and grouped by plating batch. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

sum of the diffracted intensities from all illuminated grains satisfying Bragg's law:

$$I_{hkl}(\Delta 2\theta) = \sum_j N_j^2 |F_{hkl}|^2 \text{Sinc}^2(t\vartheta) \quad (1)$$

$$\vartheta = \frac{\pi}{\lambda} \cos\theta_B(\Delta 2\theta); \Delta 2\theta = 2\theta - 2\theta_B.$$

In Eq. (1), N_j is the number of unit cells in a diffracting grain, and the summation is over all diffracting grains for the particular reflection at Bragg angle θ_B ; F_{hkl} is the structure factor for this reflection hkl , t is the film thickness, and λ is the wavelength of the monochromatic X-rays [3]. Since maximum peak intensity is difficult to measure experimentally, the integrated peak intensity, $\bar{I}_{hkl} = \int I(\theta)d(2\theta)$, which is less susceptible to experimental and statistical errors [16] and is directly proportional to the diffracting grain volume for the hkl reflection, is generally used. The integrated intensity, \bar{I}_{hkl} , is proportional to the total volume of crystalline material which contributes finite intensity to the measured Bragg peak. The full-width-at half-maximum intensity (FWHM) of the Bragg peak, β_{hkl} , can be used to determine the equivalent (effective) grain size, $\langle D \rangle_{hkl}$ along the film thickness direction through the Scherer equation:

$$\langle D \rangle_{hkl} = \frac{C\lambda}{\beta_{hkl} \cos\theta_B} \quad (2)$$

Here the carats indicate the diffraction average taken over all diffracting grains. For films with columnar microstructures, $\langle D \rangle_{hkl} = t$. It is seen that monitoring \bar{I}_{hkl} and β_{hkl} as a function of time can yield quantitative data about variations in the volume and thickness of the transforming regions associated with the particular reflection [13]. We note that using the FWHM to monitor the transformation requires more effort since the broadening contributions from all sources – such as instrumental, coherent domain size and lattice parameter dispersion terms must be separated [1].

In our current study the diffraction data analysis followed the procedures described in our previous studies [3,13], where a model that coupled time-resolved X-ray diffraction measurements to the traditional Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetics analysis [17] was reported. In the classic JMAK analysis, Eq. (3), f is the recrystallized volume fraction within the region of interest, τ_0 is the incubation time, τ is the elapsed time, m is a constant related to the dimensionality of the recrystallization, and K is a parameter encompassing nucleation

and growth rates.

$$f(\tau) = 1 - e^{-(K(\tau - \tau_0)^m)} \quad (3)$$

In addition to K and m , the parameters τ_{50} and τ_{∞} the time required to achieve 50% and 100% of the transformation, respectively, are also used to characterize the transformation. In the literature the τ_{50} parameter is the preferred metric for comparing recrystallization times of different samples [11].

For X-ray diffraction measurements the recrystallized volume fraction within the region of interest, f , is expressed in terms of the normalized change in the integrated intensity, \bar{I}_{hkl} , for a particular reflection:

$$f_{\bar{I}_{hkl}}(\tau) = \frac{\bar{I}_{hkl}(\tau) - \bar{I}_{hkl}(\tau_0)}{\bar{I}_{hkl}(\tau_{\infty}) - \bar{I}_{hkl}(\tau_0)} \quad (4)$$

Data obtained from Eq. (4) refers only to transformation within the grains diffracting into the hkl reflection employed in the measurement. For a symmetric, radial scan all of these (diffracting) grains have one member of their $\langle hkl \rangle$ vectors parallel to the surface normal of the thin film; thus the ensemble of the diffracting grains form a (discontinuous) volume with virtual fiber texture, with the fiber axis being along the $\langle hkl \rangle$ direction [18]. For the purposes of this paper we will refer to these (virtual) fiber texture sets as “texture components”. Consequently the transformation kinetics parameters, K , m , τ_0 , τ_{50} , and τ_{∞} , obtained from a diffraction-based JMAK analysis are texture-specific, and can be different for different reflections.

3. Experimental details

3.1. Sample manufacture

A standard sample metallurgy was selected based on its industrial relevance. A schematic of the standard film stack is shown in Fig. 2. The dual-layer diffusion barrier of 10 nm cubic α -Ta on 5 nm TaN (amorphous) of this standard template was physical-vapor-deposited (PVD) in an Endura sputtering system on a 0.7 mm thick, 200 mm diameter, silicon (001) wafer. Subsequently, a 50 nm Cu seed layer was deposited by sputter PVD at 10 mTorr argon partial pressure (1.33 Pa) without breaking vacuum.

The wafer was then cleaved into coupons, approximately $8 \times 8 \text{ mm}^2$, on which Cu thin films were electroplated manually in a beaker. The electroplating solution consisted of 40 g/l Cu, 10 g/l H_2SO_4 , 50 ppm Cl, with 6 ml/l commercially available Viaform® accelerator and 2 ml/l Viaform® suppressor. It was vigorously stirred during plating. An undoped, high purity Cu sheet was used as the anode. The electroplated region was confined to a circular area in the center of each coupon by masking the surface with dicing tape in which a 4 mm diameter hole had been punched.

Electroplated Cu Film	$\approx 0.4\text{--}1.5 \mu\text{m}$
Copper Seed Layer	20–50 nm
Ta Diffusion Barrier	10 nm
TaN Diffusion Barrier	5 nm
Silicon Substrate	$\approx 700 \mu\text{m}$

Fig. 2. Cross-section schematic of the standard thin-film stack used in this study.

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