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.

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 Figure 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.

II-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 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 Eqn. 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, $\bar{I}_{hkl} = \int I(2\theta)d(2\theta)$, 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 functions 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, Eqn. 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 Eqn. 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.

III- Experimental Details

III-1 Sample Manufacture

A standard sample metallurgy was selected based on its industrial relevance. A schematic of the standard film stack is shown in Figure 2. The dual-layer diffusion barrier of 10 nm cubic $F\alpha$ -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 (1.33Pa) 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

H₂SO₄, 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.

To enhance Cu nucleation, each sample was initially exposed to a low plating current density of 5.0 mA/cm² for approximately 10 seconds. Subsequently, a higher current density of 50 mA/cm² was applied. The application time of the higher current density determined film thickness: if applied for 80 seconds, an electroplated Cu layer with nominal thickness of 1.0 μm was obtained. To prevent transformation during transportation, the plated samples were immediately submersed under liquid nitrogen in a Dewar flask. Accurate film thickness values were obtained by focused ion beam milling and scanning electron microscopy (FIB/SEM) after the x-ray measurements. Some thickness values were also validated by profilometry.

III-2 X-ray Measurements

Diffraction measurements were performed at beamline X20A of the National Synchrotron Light Source at Brookhaven National Laboratory using a Huber 5020 four-circle diffractometer. A double-crystal Ge (111) monochromator was used to obtain either a 0.25 or 1 mm² incident x-ray beam spot on the sample with an energy of 9.200 keV ($\lambda=1.348$ Å). A Ge (111) analyzer crystal, placed in front of the avalanche photodiode detector, was used for high angular resolution. The incident direct beam, measured with these optics, exhibited a Lorentzian profile with a FWHM of 0.009 ± 0.001 degrees. For all samples, symmetric radial scans of the 111, 200, 220 and 311 Cu reflections were obtained; typical scan times were 5-10 minutes per reflection. The saturation of the diffracted intensities from the minor texture components (200, 220, and 311 reflections) always occurred prior to or coincided with the saturation of the diffracted intensity from dominant 111 grain volume. On this basis the monitoring of the 111 reflection intensity, $\bar{I}_{111}$, was sufficient to determine the overall recrystallization time of each film. Therefore, all tabulated references to recrystallization time, τ_{50} , are drawn from the JMAK

fittings of the 111 reflections [19]. Further details of the experimental procedure are reported in our previous articles [3, 13].

IV- Experimental Results

IV-1 Correlation between Film Recrystallization Time and Initial Film Texture:

In industrial practice it has been commonly assumed that controlling plating chemistry, plating current, and plating time would be sufficient to yield repeatable thickness and recrystallization behavior in the resulting electroplated Cu film. There are many studies that show that such control does yield electroplated films of comparable thickness [20,21]. However, we were not able to find published statistical studies that validated the uniformity of recrystallization response. Our first set of experiments was designed to test this assumption. Seven nominally identical samples were prepared under nominally identical plating chemistry, plating current, and plating time. The coupons for these samples were all cleaved from a single wafer on which a 50 nm PVD Cu seed had been deposited at 10 mTorr argon partial pressure (1.33 Pa) over a dual-layer diffusion barrier of 10 nm Ta on 5 nm TaN. The coupons were plated sequentially in the same beaker containing the same plating bath chemistry for 80 ± 1 seconds with the same plating current sequence (5.0 mA/cm^2 for 10 seconds, then 50 mA/cm^2 for 70 seconds). The samples were then transported to NSLS in liquid nitrogen, and the diffraction responses of the recrystallizing films were measured in real time. Changes in $\bar{I}_{111}$ versus time for these seven samples are shown in Figure 3. It is seen that the transformation responses for these nominally identical samples are not identical. Transformation parameters obtained from these curves through the JMAK analysis, listed in the first three columns of Table 1, show that the recrystallization times, τ_{50} , computed from the 111 integrated intensities of these "identical" samples vary by as much as $\pm 20\%$.

Comparing the intensities of the 200, 220 and 311 reflections with that of the 111 reflection it was seen that all seven electroplated films possessed strong 111 fiber textures; the 200 reflections yielded the next highest diffracted intensity for all samples. Consequently, the ratio of the integrated intensities of the 111 and 200 reflections at time zero, R_{Tx} , was used to

quantify the strength of the initial 111 texture of the electroplated film on a given coupon. These values are shown in the fifth column of Table 1: all films exhibit very strong initial 111 texture, with $R_{Tx} = \bar{I}_{111}/\bar{I}_{200}$ ratios in excess of 80:1. In untextured copper films the $\bar{I}_{111}/\bar{I}_{200}$ ratio would be approximately 2:1 (JCPDS #040836).

Comparison of the second and fifth columns of Table 1 shows that lower initial film texture ratios, R_{Tx} , correlate with faster sample recrystallization times, τ_{50} (Fig. 1; black squares). The spread of R_{Tx} values is quite similar to that of the τ_{50} values; in both cases the standard deviation is approximately 23% of the mean value. We also note that in the JMAK analysis, Eqn. 3, the constant related to the dimensionality of the recrystallization, m , shows the smallest standard deviation, approx. $\pm 6\%$, while the K parameter, encompassing nucleation and growth rates, shows variability in excess of 100%.

IV-2 Effect of Cu Seed Layer Texture:

Since the variability in the τ_{50} values listed in Table 1 cannot be ascribed to the plating parameters, other possible causes were investigated. In a previous study where full wafers were used, in the past literature several groups, including Ueno and co-workers, ascribed such differences to variability in thickness [7-10, 12]. In our work, no variation of plating power across the small plating area is expected, and profilometry measurements and FIB cross sections coupled with SEM analysis confirmed that uniform thickness was achieved for all coupons. Since it is also well known that the initial texture of the electroplated Cu films can be influenced by the texture of the Cu seed layers [7-10, 12] through the “templating” or “texture inheritance” mechanisms [12], texture variation within the seed layer was identified as a second possibility. To test this hypothesis, 111 peaks of the Cu seed layers of all seven samples were measured from the masked regions of each coupon (Figure 4). These protected seed layer regions were stable at room temperature and did not show any evidence of transformation during our experiments. On the other hand, PVD seed and electroplated Cu film layers could not be distinguished in cross-sectional FIB/SEM micrographs after the recrystallization of the overlying film, indicating consumption of the seed layer. Figure 4 shows that both maximum

and integrated intensities of the 111 peaks of the seed layers, as well as their FWHM values, β_{hkl} , showed significant variability between nominally identical coupons.

The (maximum) difference in integrated intensities of the weakest and strongest 111 reflections in Figure 4, measured from the seed layers of samples PVD-10mT-1 and PVD-10mT-5 respectively, is 36% of the overall mean integrated intensity from all seven coupons, with one standard deviation corresponding to 12% of this mean value. These variations can be caused by variations in the film thickness, film texture, or both of film thickness and texture. In general, while a slight variation of PVD seed thickness from the center to the edge of a wafer is observed, $\pm 20\%$ variability in film thickness is not expected in coupons cut from adjacent portions at center of the wafer. SEM/FIB imaging (Figure 5) also indicated a uniform Cu seed.

Based on these observations, we ascribed the variations in the 111 peaks to the changes in the texture of the underlying Cu seed and concluded that the repeatability of the texture of the electroplated film was strongly influenced by the repeatability of the texture of the seed layer. This conclusion was then tested by adapting the approach of Clevenger, *et al.* [22], who modulated the stress and microstructure of Ta films by varying the argon partial pressure in the chamber, to Cu seed layer deposition.

In this series of tests 50 nm thick Cu seed layers were grown using physically vapor deposited (PVD) in an Endura sputtering system on two 0.7 mm thick, 200 mm diameter, silicon (001) wafers at 2 mTorr and 25 mTorr of argon partial pressure (0.267 Pa, 3.33Pa), respectively. These wafers were otherwise identical to the standard PVD wafer described in section A. The $8 \times 8 \text{ mm}^2$ coupons cleaved from these two wafers were then electroplated with Cu using the bath chemistry and electroplating procedures described previously. Consequently, the only difference between these samples and the ones used to populate Table 1 is the argon partial pressure used during seed deposition. Diffraction spectra from the seed layers, and the corresponding transformation curves of the electroplated Cu films are shown in Figures 6 a-b, and 6 c-d for the 2mTorr and 25mTorr seed wafers, respectively.

Comparison of Figures 6-a and 6-b shows that the 111 reflections obtained from various coupons of the wafer with the PVD Cu seed film deposited at the higher Ar partial pressure exhibited much better uniformity. The Cu seed layer deposited at the lower Ar partial pressure had a lower average 111 intensity, with higher coupon-to-coupon variability. The mean integrated intensity/standard deviation computed from the five samples shown in Figure 6-b is 3.64 ± 0.4 . The corresponding value for Figure 6-a are 2.8 ± 1.0 . The variability of the transformation curves for the electroplated Cu films plated on these two wafers correlated with the variability of the corresponding $\bar{I}_{111}$ values of the seed layers (Figures 6-c,d and Table 2). The variability of the average texture ratios at time zero, R_{Tx} , also correlates with the variability of the corresponding $\bar{I}_{111}$ values of the seed layers (Figure 1, blue circles). Consequently, our conclusion in section A, linking the variability in room-temperature recrystallization response to the variability in seed texture is justified.

Table 2 also shows that the Cu films electroplated on the PVD seed layers deposited at lower Ar partial pressure, PVD-2mT, were more weakly 111 textured than their high pressure, PVD-25mT, counterparts. This corresponded to significantly faster average recrystallization times.

IV-3 Influence of Plated Film Thickness on the Initial Film Texture Ratio

In the literature there are many studies that show an inverse correlation between the thickness of an electroplated film and its room temperature transformation time, τ_{50} [20,21]. As we noted earlier, the 50 nm thick Cu seed layer films were stable at room temperature and did not show any evidence of transformation during our experiments. These seed layers were very highly 111 textured; no other reflections yielded finite intensities. Based on our observations in sections A and B, we postulated that increasing the thickness of the electroplated film probably resulted in a decrease in the texture ratio at time zero, R_{Tx} , which in turn, resulted in a faster transformation rate. To test this hypothesis we used a set of samples which were electroplated on coupons cut from the same wafer as the films of Table 1, and therefore possessing nominally identical seed and barrier layer structures. The electroplating process used nominally identical plating current and plating bath chemistry as well. The range of plated film thicknesses was

accomplished by varying the plating time between 20 to 80 seconds. Sample designations and transformation parameters are shown in Table 3. The numerical part of the sample names (PVD-#) indicates the duration of sample exposure to the 50 mA/cm² current density (in seconds) during electroplating. The film thickness values listed in column 2 were measured by FIB/SEM analysis after the room temperature recrystallization measurements were completed. Comparison of the second and third columns of Table 3 shows that the initial texture ratio of these films, $R_{Tx} = \bar{I}_{111}/\bar{I}_{200}|_{\tau=\tau_0}$, monotonically decreases with increasing film thickness. The R_{Tx} parameter decreases nearly 7-fold as thickness increases 2.5 times, from 0.4 μm to 1.0 μm . Thus, the strength of the initial 111 texture of an electroplated Cu film changes dramatically with film thickness for films with PVD seed layers. Comparison of the third and fourth columns of Table 3 show that the 50% transformation time, τ_{50} , decreases monotonically with decreasing texture ratio at time zero, R_{Tx} . These data fit the trend, established by samples described in Sections A and B, of the dependency of τ_{50} on R_{Tx} ; they are depicted by red triangles in Figure 1. The thinner electroplated films of this study have the highest texture ratios, and the slowest transformation times among the samples we studied. We note that the thinnest electroplated films of this set, 0.4 and 0.55 μm in thickness, respectively, did not transform during the time available to us at the synchrotron, even though some increase in the 111 intensity was observed [13].

The Cu film electroplated on sample PVD-80 of Table 3 should be nominally identical to the samples described in Table 1. All of these films were plated on coupons from the same wafer, with the same chemistry and voltage/current regimen; in all eight cases the final electroplated films were nominally 1 μm thick. There was, however, a six month gap between the two sets of experiments; a new bath, with identical composition, had to be mixed for the second set. We see that the R_{Tx} value of sample PVD-80 is approximately 2x that of the average R_{Tx} value listed in Table 1. Consequently, even minor composition variations in nominally identical plating baths can result in major changes in the time-zero texture ratio of electroplated films and their subsequent recrystallization behavior.

At this point comparing the transformation kinetics parameters, K , m , τ_{50} (Eqn. 3, 4) listed in Tables 1, 2 and 3 is also useful. In Tables 1 and 2, the magnitudes of the deviations in the K parameter are similar to their average values. Consequently, the K parameter cannot be used to extract useful information about the transformation for these cases. The average value of the “ m ” parameter from the PVD-10mT samples (Table 1) is similar to the average “ m ” of the PVD-2mT samples (Table 2): 3.3 ± 0.4 and 3.2 ± 0.2 , respectively, but not of the PVD-25mT samples, $m = 1.6 \pm 0.3$. Both the 2mT and 10mT samples exhibit large variations in τ_{50} whereas better uniformity in τ_{50} was observed in the 25mT samples. Thus, it is possible that $m \approx 3$ (typically corresponding to 3-D growth for growth in a fully nucleated material) may be representative of greater microstructural variability than in samples where $m < 2$ (typically corresponding to 2-D growth). However, the parameters K , m , τ_{50} for the thickness study samples (Table 3) show a different trend. For this set the seed Cu layer was also deposited at 10 mT argon pressure. The deviation in the K values, between 10 to 40% of the mean value, is significantly smaller than the deviations listed in the previous tables. The m value for the PVD-80 sample, (electroplated Cu film thickness $\approx 1 \mu\text{m}$) is 1.8, indicating 2-D growth, which is very different from the average m parameter for Table 1, where all samples had nominally $1 \mu\text{m}$ thick electroplated Cu layers. As noted before, the samples described in Table 3 were plated at a different time, but with a nominally identical bath chemistry and electrodeposition parameters. Consequently, it appears that the JMAK kinetics parameters K , m , are not correlate-able across plating baths in our study. While we also observe large variations in the texture ratio between baths, the correlation between τ_{50} and R_{Tx} is obeyed (Figure 1). Consequently, only these parameters will be used in the remainder of this study.

IV-4 Controlling Recrystallization of Electroplated Cu Films through Seed Texture

Manipulation

The utilization of the atomic layer deposition (ALD) process for depositing a thinner conformal Cu seed layer has been the subject of much recent research [5, 23]. This technique is based on a self-limiting surface reaction wherein suitable precursors are pulsed over the substrate surface to form a single atomic monolayer. This is followed by a purge of the ALD chamber followed

with a subsequent pulse, which forms another identical monolayer on the previous one. The ALD technique allows very precise control of the seed layer thickness but the deposition speed is quite slow, limiting the maximum Cu seed layer thickness to below 20 nm for the process we used. Our ALD Cu seeds were deposited employing AbaCus (Air Liquide, Inc.) and plasma-activated hydrogen as reactants in a room temperature process. The use of room temperature processing avoided the significant copper agglomeration which is typical of higher temperature deposition processes [23]. The ALD deposition procedure included a vacuum break between the barrier layer and seed deposition steps.

We prepared two types of wafers which incorporated an ALD seed layer within the sample stack (Table 4). The first wafer, termed the ALD sample (1st row, Table 4) contained only a single 20 nm thick ALD seed layer, upon which the blanket Cu film was directly electroplated. Synchrotron x-ray measurements from this bare ALD seed yielded only an extremely broad and extremely weak, barely discernible 111 reflection (Figure 7-a, bottom black trace). The 200, 220, and 311 reflections could not be resolved. In addition, the grains within the ALD Cu layer could not be resolved in FIB/SEM cross-sectional photographs. Using the Scherer Equation (Eqn. 2) the average Cu grain size within the ALD layer was estimated to be less than 2 nm.

The initial texture ratio of the Cu film, R_{Tx} , electroplated on the ALD seed layer was much weaker than the values for the films electroplated on PVD seed layers summarized in Tables 1 and 2. The τ_{50} transformation time for the Cu film electroplated on ALD Cu seed, 2.8 hours, was also much faster than any other film we studied. The third entry of Table 4 lists the transformation characteristics of a Cu film of comparable thickness, plated on our standard 50 nm PVD Cu seed with the same batch as the ALD coupons using identical plating parameters. Comparison of the R_{Tx} and τ_{50} values for the ALD and PVD samples in Table 4 clearly shows the importance of seed layer texture in modulating the transformation speed. This is also seen in Figure 7-b, where the variation of integrated intensity with time plots of this batch of samples are shown.

To further study the effect of seed layer texture templating on transformation kinetics, Cu was electroplated on coupons cleaved from the dual-seed wafer, in which a nominally 20 nm ALD

Cu seed layer was deposited on 30 nm PVD Cu, sputtered at 10 mTorr argon partial pressure (1.33Pa). We expected a more 111 textured ALD seed layer surface through templating from the highly textured PVD Cu layer. The cross-sectional image of this structure is shown in Figure 8. Both layers are discernible, indicating that they have different microstructures. The ALD Cu grains are not resolved. The 111 reflection for this composite seed layer is shown in the middle (red) trace of Figure 7-a. This profile contains the depth-averaged contributions from both seed layers and shows that, on the average, the seed 111 intensity is much stronger than that of the bare ALD layer, but $1/3^{\text{rd}}$ weaker than the 50 nm PVD seed. Figure 7-a also shows that the 111 peak position of the composite Cu layer is shifted to lower 2θ , compared to that of the 50 nm PVD Cu seed, indicating that the plane spacing of the composite layer in the direction of the film surface normal is larger, indicating a possible change in the plating residual stress acting on the film

Even though we could not resolve the specific texture of the top (ALD) surface of the composite seed layer independently, some templating must have occurred: The R_{Tx} value for the electroplated Cu film was 3x that of the corresponding film plated on the bare ALD seed layer (Table 4, middle row), with a correspondingly longer transformation time (Figure 7-b). The τ_{50} vs. R_{Tx} data for all three films listed in Table 4 also follow the general trends established in Figure 1.

IV-5 Film Thickness Effect in Transformation of Cu layers Plated on ALD Seed:

Comparison of Tables 1 and 4 shows that the nominally 1 micrometer thick Cu films electroplated on non-textured ALD seed layers transformed much faster than similar films plated on highly 111 textured PVD Cu seed layers. To check if the same effect permitted the transformation of thinner electroplated layers, Cu films with thicknesses similar to those listed in Table 3 were electroplated on coupons cleaved from the wafer with 20 nm ALD Cu seed layer. The results from this study are listed in Table 5, where the sample naming convention is identical to that used in Table 3: ALD-# indicates that the Cu film was electroplated on ALD Cu seed and the # indicates the duration (seconds) of high plating current application.

The third column of Table 5 shows that the time-zero texture ratios, R_{Tx} , for all ALD-# samples are two to three orders of magnitude lower than the corresponding values for the PVD films listed in Table 3. All of the samples listed in Table 5 transformed. The 0.33 μm thick electroplated Cu film (sample ALD-20) was 50% transformed in 48 hours. In contrast, the PVD-20 nm film listed in Table 3 did not transform at all in 150 hr. The actual thickness of the electroplated film for sample ALD-40 (Table 5) is slightly lower than that of sample PVD-60. However, the τ_{50} for sample ALD-40 is an order of magnitude faster. Thus, we conclude that the critical film thickness for room temperature recrystallization of Cu is strongly dependent on the time-zero texture ratio, R_{Tx} , of the electroplated film.

Table 5 also shows that for Cu films with very low initial texture ratios, τ_{50} decreases for a modest increase in R_{Tx} in this range (Figure 1, the green inverted triangles, the green dashed line) which is opposite of the trend established by all of our previous samples .

IV-6 Studies with Other Modulators of Texture

Table 6 shows three further studies where the initial texture ratio was changed by modifying the seed layer. The seed stack for the first wafer consisted of 20 nm of Co evaporated on 30 nm of PVD Cu seed. The final Cu layer was directly electroplated on the Co layer. The seed stack for the second wafer consisted of 20 nm of Cu evaporated on 30 nm of PVD Cu seed. In the third wafer a single, 10 nm thick, β -Ta layer was used as the diffusion barrier, upon which the standard 50 nm thick Cu PVD seed layer was deposited. The Cu films electroplated on these wafers were significantly thicker. For all three samples the initial texture ratios, R_{Tx} , were greater than the critical texture ratio, $R_{Tx}^* \sim 7$. R_{Tx} vs. τ_{50} data from all three wafers conformed to the general relationship on the right side of R_{Tx}^* in Figure 1.

IV-7 Effect of Laboratory vs. Industrial Plating

The samples listed in Tables 1-6 made use of small Si coupons, where the Cu was electroplated manually in a beaker on a bench top. To see if the results of this manual process were industrially relevant, full 8" Si (001) wafers, processed through the standard PVD Cu seed deposition stage, were sent to a vendor for electroplating; an industrial grade (undisclosed

chemistry) Cu electroplating process was used. The results of this study are summarized in Table 7. Here the number in the sample name (I-PVD-#) corresponds to the target film thickness in nanometers. FIB measurements showed that actual films were approximately 40% thicker than the nominal values requested, but that these were uniform across the wafer. X-ray analysis revealed that these films were strongly 111 textured as well. This initial texture decreased 10x as film thickness increased from 0.55 μm to 1.15 μm , which is similar to our observations in the hand-plated PVD samples (Table 3). This texture drop corresponded to a 6x decrease in recrystallization time. R_{Tx} vs. τ_{50} data from all four wafers conformed to the general relationship on the right side of R_{Tx}^* in Figure 1.

Table 7 shows that correlations established between film thickness, film texture, and recrystallization time using laboratory processes are also applicable to industrial processes.

Finally we note that in our studies we did not explicitly strive to monitor and control impurity concentrations, such as oxygen, in the plating baths or deposition chambers used to manufacture our samples. As described above, to ensure the broadest coverage of plating parameters possible, we did not limit sample manufacture to one single run, a single process, nor to one single facility. The effect of initial texture on the transformation response from all of our specimens is very consistent, indicating that contamination, to a first approximation, is not a primary driver of initial texture, or τ_{50} , as long as nominal care, standard in industrial processing, is maintained during sample manufacture.

V Summary and Conclusions

The data tabulated in Tables 1-7 show that the strength of the 111 texture component of an electroplated Cu film at time zero is critical in the development of any subsequent room temperature microstructural transformation. Any process which modifies texture of the seed layer, or the texture of the electroplated film at time zero, will change the recrystallization response. A convenient metric to define the texture strength is the ratio of the integrated intensities from 111 and 200 reflections at time zero, $R_{Tx} = \bar{I}_{111}/\bar{I}_{200}|_{\tau=\tau_0}$. For a Cu film with randomly oriented grains the R_{Tx} parameter should be equal to 2.0. Higher values indicate

stronger 111 texture, with more grains having a $\langle 111 \rangle$ direction parallel to the surface normal of the film than expected within a random orientation distribution.

The data plotted in Figure 1 show that the x-ray JMAK 50% transformation time, τ_{50} , of the 111 texture component can exhibit two distinct responses based on the value of R_{Tx} : For electroplated Cu films with R_{Tx} greater than 7 or so, τ_{50} increases exponentially with increasing R_{Tx} . For films with $R_{Tx} < 7$ the opposite trend is observed. Thus, we define a critical initial texture ratio, $R_{Tx}^* \cong 7$, which separates the two regions where the variation of τ_{50} with R_{Tx} is opposite.

The majority of samples tested in this study had R_{Tx} values greater than 7 (due to textured seed layers) and transformed relatively slowly at room temperature. The thinnest films plated on textured seed layers had the highest R_{Tx} values ($R_{Tx} > 1400$), and these did not transform at all. We observed that the most effective means of manipulating R_{Tx} was through controlling the texture of the Cu seed layer. Cu films plated on highly textured seed layers were also highly textured, most probably through an efficient templating mechanism [12]. R_{Tx} values for these electroplated Cu layers decreased with increasing film thickness, with an attendant increase in transformation speed. For plated films with $R_{Tx} > 7$, processing steps which did not change R_{Tx} did not influence τ_{50} values. For example, plastic flow induced in the Cu film immediately after plating by quenching identically plated coupons in 1-liquid nitrogen, 2-dry ice and 3-ice-water did not significantly change the R_{Tx} values, and no change in the JMAK 50% transformation time, τ_{50} , was observed [1].

Cu films electroplated on untextured nano-grained Cu seed layers exhibited R_{Tx} values between 4 and 6. All of these samples, including a 330 nm thick plated film, completely recrystallized at room temperature at much faster rates than those with $R_{Tx} > 7$ (Fig. 1, Table 5). In contrast, the 400 and 550 nm thick films plated on textured seed layers (Table 3) did not transform: the former exhibited no recrystallization, and the latter had barely gotten past incubation after 180 hr at room temperature. For a film of given thickness, this observation indicates that the transformation can be controlled by varying R_{Tx} , for example by using seed layers with the desired texture. We also conclude that changing the texture changes the

energetics of recrystallization; surface and strain energy minimization terms which depend on texture are just as important as grain boundary energy minimization considered in reference 7.

The critical texture ratio also delineates two regions where the variation of R_{Tx} with film thickness displays opposite behaviors (Figure 9-a). This may be ascribed to the templating process which yields an initially untextured plated Cu layer on the seed, which then recrystallizes rapidly during plating to minimize grain boundary and surface energy terms in the presence of a residual stress field. This forms mildly textured plated films by the end of the plating process [24]. In contrast, the first few Cu layers forming on textured seed are already highly 111 textured. As the film grows thicker, minimization of strain energy causes the formation of some 001 type grains, causing the (thicker) films to have (relatively) lower R_{Tx} values [24]. Since, for both types of films, the 50% recrystallization time, τ_{50} , shows a similar dependency on electroplated film thickness (Figure 9-b), the texture data is critical in identifying the mechanisms responsible for room temperature recrystallization. We are working on this problem and will report it in a further manuscript.

In contrast to the very definite relationship between the texture ratio R_{Tx} and the 50% transformation time, τ_{50} shown in Figure 1, we could not correlate the JMAK kinetics parameters K , m to verifiable microstructural changes when the plating bath or other deposition parameters were changed. While these parameters might be useful in analyzing transformation within one sample batch, their utility in a general study appears to be limited.

In summary, our work demonstrates that tightly controlling process parameters, such as the bath chemistry, electrodeposition current, voltage and application times, to control the total thickness of an electroplated Cu film is insufficient to control its room temperature recrystallization response. Local variations in the texture of the seed layer can cause just as large variations in the transformation times as thickness variations. Ensuring uniform texture of the seed layer will yield uniform room temperature recrystallization response for blanket Cu films. In addition, electroplating on a seed layer with very low texture enables the recrystallization of very thin films which would otherwise not recrystallize, and significantly speeds up the recrystallization of thicker films. The texture ratio is a simple parameter to

measure on a manufacturing line [25] and can be a good parameter to monitor for process control purposes.

Acknowledgements

This work was funded by the Semiconductor Research Corporation and supported by their partners at IBM Research Yorktown, Global Foundries, and SUNY Albany. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

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Figure 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.

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

Figure 3: Temporal variation of the integrated intensities of the 111 reflections, $\bar{I}_{111}$, for a series of nominally identical plated films from the same wafer. These electroplated films showed a greater than 20% spread in recrystallization time, τ_{50} . The specimen numbers do not represent the order of plating.

Figure 4: 111 Bragg peak profiles of the Cu seed layers for coupons PVD-10mT-1 through PVD-10mT-7 (Table 1).

Figure 5: FIB/SEM cross-section of the PVD seed layer-diffusion barrier (H2) stack from the wafer used in the repeatability study with samples of Table 1. The average thickness of the seed layer (H1-H2) is 51 ± 4 nm.

Figure 6: 111 Bragg peak profiles measured from PVD Cu seed layers deposited under 2 mTorr (0.267 Pa) **(a)** and 25 mTorr (3.33Pa) **(b)** argon partial pressures, respectively. In both cases the Cu seed layers exhibited strong 111 texture. Variation of the 111 integrated intensity, $\bar{I}_{111}$, with time for Cu films electroplated on the PVD Cu seed layers deposited at 2 mTorr **(c)** and 25 mTorr of argon partial pressure **(d)**. Transformation parameters obtained from JMAK analysis of these curves are listed in Table 2.

Figure 7-a: 111 Bragg peak profiles measured from copper seed layers deposited by the ALD, PVD, and dual-layer ALD/PVD processes (Table 4). **(b)** Variation of the 111 integrated intensity, $\bar{I}_{111}$, with time for Cu films electroplated on ALD, PVD, and dual-layer seeds.

Figure 8: FIB/SEM of the cross-section of the dual layer seed (Table 4) where nominally 20 nm of ALD Cu was deposited on 30 nm of PVD Cu seed. The ALD Cu grains are not resolved.

Figure 9: Variation of the texture ratio at time zero (R_{Tx}) **(a)** and 50% recrystallization time **(b)** with the thickness of Cu films electroplated on PVD and ALD seed layers. In both figures the dashed lines describe least-squares exponential functions fitted to the data. The first τ_{50} point (red square) in Figure 9-b for the electroplated Cu films plated on PVD seed is an extrapolated value obtained from the fitted function to the first three data points.

LIST OF TABLE CAPTIONS

Table 1: JMAK recrystallization parameters, τ_{50} , K , m , and film texture ratio at time zero, R_{Tx} , seven nominally identical specimens. The recrystallization parameters were computed from the data shown in Figure 3. The specimen numbers do not represent the order of plating.

Table 2: JMAK transformation parameters and zero-time texture ratios (R_{Tx}) of Cu films electroplated on 50 nm PVD Cu seed layers deposited under low (2 mTorr; 0.267 Pa) and high (25 mTorr; 3.33Pa) Argon partial pressures.

Table 3: JMAK recrystallization parameters, τ_{50} , K , m , and film texture ratio at time zero, R_{Tx} , as a function of plated film thickness. All samples utilized here were cleaved from a wafer with a 50 nm PVD seed layer deposition at 10 mTorr (1.33Pa) Ar partial pressure, and were electroplated under nominally identical conditions for gradually longer times (20 to 80 seconds).

Table 4: Transformation parameters of Cu films electroplated on seed layers incorporating an atomic layer deposited (ALD) Cu layer. For both ALD and PVD-ALD films, the seed layer on which the final Cu layer was electroplated was nominally 20 nm thick ALD Cu. The diffusion barrier layers for all three sets of samples consisted of 10 nm α -Ta on 5 nm TaN films as shown in Figure 2.

Table 5: Dependence of the 50% recrystallization time, τ_{50} , and the time-zero texture ratio, R_{Tx} on electroplated film thickness when an ALD Cu layer is used as seed.

Table 6: JMAK Recrystallization parameters for Cu films electroplated on evaporated cobalt and copper capped seed layers (first two rows). For these samples the standard diffusion barrier, 10 nm α -Ta on 5 nm TaN, was used. The seed layer of the sample described in the last row, 50 nm thick PVD Cu, was deposited on a single 10 nm thick layer of β -Ta.

Table 7: Dependence of the 50% recrystallization time, τ_{50} , and the time-zero texture ratio, R_{Tx} on electroplated film thickness for films electroplated on 50 nm PVD seed layers by a (proprietary) industrial full wafer plating process.

Tables

Coupon ID	τ_{50} (hours)	$K(x\ 10^{-4})$	m	R_{Tx}
PVD-10mT-1	21±2	0.54±0.38	3.09±0.23	145±11
PVD-10mT-2	21 ±2	1.1±0.73	2.86±0.21	139±10
PVD-10mT-3	17±2	0.67±0.86	3.24±0.44	107±7
PVD-10mT-4	15±2	0.93±0.5	3.28±0.20	99±5
PVD-10mT-5	15±2	0.69±.76	3.44±0.41	95±6
PVD-10mT-6	14±2	0.97±0.84	3.38±0.32	95±6
PVD-10mT-7	12±2	4.1±2.6	3.03±0.26	77±5
Average	17±4	1.28±1.25	3.2±0.2	109±25

Table 1

Sample ID	Argon PP (mTorr)	τ_{50} (hours)	R_{Tx}	$K(x\ 10^{-4})$	m
PVD-2mT	2	7.6±2.0	27±14	14±9	3.3±0.4
PVD-25mT	25	8.7±1.2	44±9	236±101	1.6±0.3

Table 2

Sample ID	Film Thickness (μm)	R_{Tx}	τ_{50} (hr)	$K(x\ 10^{-4})$	m
PVD-20	0.4±0.06	1736±376	--	--	--
PVD-30	0.55±0.07	1476±302	--	--	--
PVD-40	0.7±0.01	854±87	150±10	2.9±0.3	1.56±.02
PVD-60	0.8±0.03	534±77	59±6	3.2±0.4	1.89±.03
PVD-80	1.0±0.06	267±32	40±10	10±0.4	1.80±.01

Table 3

Sample ID	Seed Layer Stack	τ_{50} (hours)	R_{Tx}	Seed $\bar{I}_{111}$ (ct/kmon)	Electroplated Film Thickness (μm)
ALD	20 nm ALD	2.8 $\pm$ 0.3	6 $\pm$ 1	3E-4 $\pm$ 7E-5	1.35 $\pm$ 0.12
PVD-ALD	20 nm ALD on 30 nm PVD	6.4 $\pm$ 0.4	19 $\pm$ 1	0.37 $\pm$ 8E-3	1.39 $\pm$ 0.09
PVD	50 nm PVD	12.4 $\pm$ 0.8	112 $\pm$ 10	1.36 $\pm$ 0.16	1.37 $\pm$ 0.10

Table 4

Sample ID	Film Thickness (μm)	R_{Tx}	τ_{50} (hours)
ALD-20	0.33 $\pm$ 0.06	4.0 $\pm$ 0.2	48 $\pm$ 5
ALD-40	0.64 $\pm$ 0.05	5.1 $\pm$ 0.2	12.0 $\pm$ 1.2
ALD-60	0.85 $\pm$ 0.08	5.9 $\pm$ 0.1	8.2 $\pm$ 0.8
ALD-80	1.00 $\pm$ 0.11	6.4 $\pm$ 0.1	7.4 $\pm$ 0.5

Table 5

Sample ID	Diffusion Barrier	Seed Layer Stack	τ_{50} (hours)	R_{Tx}	$\bar{I}_{111}$ of Seed Layer (ct)	Plated Film Thickness (μm)
PVD-Co	standard	20 nm Evap Co on 30 nm PVD Cu	8.4 $\pm$ 0.9	31 $\pm$ 2	0.35 $\pm$.01	1.49 $\pm$ 0.16
PVD-Evap-Cu	standard	20 nm Evap Cu on 30 nm PVD Cu	7.6 $\pm$ 0.7	25 $\pm$ 4	0.43 $\pm$.01	1.73 $\pm$ 0.29
PVD- β -Ta	10 nm β -Ta	50 nm PVD	9.1 $\pm$ 0.2	55 $\pm$ 4	4.0 $\pm$ 0.25	1.34 $\pm$ 0.16

Table 6

Sample ID	Film Thickness	τ_{50} (hours)	R_{Tx}
I-PVD-400	0.55 $\pm$ 0.03 μm	25 $\pm$ 1	335 $\pm$ 19
I-PVD-600	0.85 $\pm$ 0.05 μm	4.4 $\pm$ 0.1	37.6 $\pm$ 9.3
I-PVD-800	1.14 $\pm$ 0.07 μm	5.5 $\pm$ 0.2	33.4 $\pm$ 7.9
I-PVD-1000	1.48 $\pm$ 0.02 μm	4.0 $\pm$ 0.1	14.7 $\pm$ 0.3

Table 7

Figure_1

Figure_2

Figure_3

Figure_4

Figure_5

Figure_6a

Figure_6b

Figure6c

Figure6d

Figure_7a

Figure_7b

Figure_8

Figure9a

(a)

Figure9b