Stress development during the electrodeposition of copper from additive-free, acidic CuSO₄ electrolyte was analyzed by dynamic stress analysis, an in situ characterization technique that combines electrochemical impedance spectroscopy with cantilever curvature. Two sources of stress account for the dynamic stress behavior in the frequency range of 0.1 Hz to 25 Hz. The high frequency region is controlled by electrocapillarity (charge-induced stress). The stress is 180° out of phase with the input potential, and its amplitude is relatively small. Low frequency is dominated by the growth stress of the Cu film, which under the conditions examined here is tensile. The amplitude of the stress response increases with decreasing frequency and its phase angle shifts from +180° to +90°.

Both of these transitions are potential dependent and can be simulated from the electrochemical impedance, making use of separate stress-charge coefficients for double layer charging and Cu deposition. Since these stress-generating mechanisms have dramatically different frequency dependencies, Cu deposition is a nice demonstration that highlights the attributes of DSA; i.e., using frequency to separate the various stress contributions.

Although most agree that the final steady-state stress is subject to competing processes that simultaneously generate both tensile and compressive stress, determining the exact mechanisms that generate these stresses, particularly the compressive stress, is still an active area of research. Chason has proposed a grain boundary insertion mechanism where compressive stress is generated by the diffusion of atoms into the grain boundary as the film grows. The driving force is the non-equilibrium conditions on the surface during deposition that lead to an increase in the chemical potential of adatoms relative to equilibrium conditions. This mechanism accounts for both residual compressive stress in the film and the observed relaxation of compressive stress when deposition is interrupted. This is nicely demonstrated for Sn deposition where the average stress decays to near zero when the growth is paused and then returns to the same value after the growth is resumed, regardless of film thickness. Although models have been developed that treat steady-state stress as a dynamic competition between tensile and compressive stress generation mechanisms that are largely governed by atomic mobility, microstructure, and deposition rate, a steady-state stress measurement will simply reflect the influence of the dominant process in the time-scale of the experiment and provide little understanding of possible stress relaxation mechanisms or final stress state.

Electrochemical impedance spectroscopy (EIS) is often used to separate electrochemical processes with different characteristic time constants. In EIS, a sinusoidal voltage signal (typically of the order of a few mV), superimposed on an applied dc voltage, is applied to an electrochemical system and the current response is measured. The frequency of the ac voltage signal is varied so that different processes can be deconvolved, based on the different frequency-dependent impedance associated with them. Dynamic stress analysis (DSA) is similar to EIS, however in addition to the current, the cantilever curvature is measured simultaneously occurring stress-generating faradaic reaction and electrocapillarity response. DSA should be sensitive to not only the stress generating mechanisms that contribute to the steady state stress but to relaxation processes that may occur as well.

Experimental

The stress was measured with an optical cantilever curvature technique that can be used during deposition to determine the real-time stress evolution. The cantilever was a borosilicate glass (Schott North America, Inc.) strip measuring 60 mm × 3 mm × 0.108 mm. The

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The relationship between the force per cantilever beam width, $\Delta F$, exerted by processes occurring on the electrode surface and the change in the radius of curvature of the cantilever, $\Delta R$, is given by Stoney’s equation:

$$\Delta F = \frac{E \cdot h^2}{6(1 - \nu)} \Delta R$$  \[1\]

where $E$, $\nu$, and $h$ are the Young’s modulus, Poisson ratio, and thickness of the glass substrate respectively. When the force on the cantilever is due to surface processes, $\Delta F$ is equal to changes in the surface stress, $f$. When the force on the cantilever is the result of bulk processes, such as metal deposition, then $\Delta F$ is equal to the stress-thickness product, $\sigma h_f$, i.e., the average biaxial film stress, $\sigma$, multiplied by the thickness of the film, $h_f$. Since the stress in polycrystalline films is generally not uniform through its thickness, the average stress is an integration of the stress distribution over the thickness of the film,

$$\sigma = \frac{1}{h_f} \int_0^{h_f} \sigma(z) \, dz$$  \[2\]

where $\sigma(z)$ is the in-plane stress in the film at a distance $z$ from the substrate.

The electrolyte was 1.8 mol/L H$_2$SO$_4$ containing 0.1 mol/L CuSO$_4$ and was prepared using 18 MΩ cm ultrapure water. The counter electrode was a platinum foil placed in the same solution and parallel to the working electrode. The reference electrode was a saturated mercury-mercurous sulfate electrode (SSE) that was separated from the working compartment by a Vycor-tipped bridge filled with saturated K$_2$SO$_4$ solution. Potential control was maintained using a potentiostat. The electrolyte was initially purged with ultra pure argon, and flow was maintained in the headspace. Prior to making a measurement, the Au cantilever electrode was cycled between −0.4 V and +1.0 V at 100 mVs$^{-1}$ until a reproducible voltammogram was obtained. The potential was then stepped to the desired deposition potential. Following deposition, the Cu was anodically dissolved from the cantilever at a potential of 10 mV to 20 mV positive of the Cu open circuit potential. Once the Cu was completely stripped, the Au cantilever was once again cycled until a reproducible voltammogram was obtained. Following voltammetry, the laser beam returned to the initial start position on the PSD, indicating that the Au surface had not been altered by the deposition/stripping process. All measurements were made at ambient temperature.

**D.S.A derivation.**—In an EIS experiment the system responds to the application of a sinusoidal signal, e.g.: $E = E_{dc} + E_0 \exp(i\omega t)$, where $E_{dc}$ is the dc potential, $E_0$ is the signal amplitude, $\omega$ is the angular frequency, and $j = \sqrt{-1}$. $E_0$ is sufficiently small so that the current response is linear and has the form $I = I_{dc} + I_0 \exp(i(\omega t + \phi))$, where $I_{dc}$, $I_0$, and $\phi$ are the dc component, amplitude, and phase-angle of the current with respect to the potential, respectively. We use the convention that a signal that lags the input signal has a negative phase angle. The ratio of the input ac voltage to the output ac current is a complex quantity called the electrochemical impedance ($Z_e$),

$$Z_e = \frac{E_0 \exp(j\omega t)}{I_0 \exp(j(\omega t + \phi))} = Z_{e,0} \exp(-j\phi_e)$$  \[3\]

The magnitude of the impedance, $Z_{e,0}$ is equal to the amplitude of the potential divided by the amplitude of the current ($E_0/I_0$). The electrochemical impedance has a negative phase angle, which is consistent with standard electrochemical convention.

In a similar fashion, the force on the cantilever, $F$, which gives rise to the curvature, also has the form $F = F_{dc} + F_0 \exp(i(\omega t + \phi))$, where $F_{dc}$, $F_0$, and $\phi_F$ are the dc component, amplitude, and phase-angle of the force response with respect to the potential, respectively (although $F$ is actually $\Delta F$, as a result of some unknown initial curvature, we will use the symbol $F$). In analogy with the electrical impedance, a stress impedance $Z_e$ can be defined. However, we prefer to employ its reciprocal, the stress admittance $Y_e$, defined as

$$Y_e = \frac{F_0 \exp(j(\omega t + \phi_F))}{E_0 \exp(j\omega t)} = \frac{F_0}{E_0} \exp(j\phi_F)$$  \[4\]

$Y_e$ has units of N/(Vm). Since the charge density has a direct impact on the stress response, it is useful to have an analytical expression for the ac charge, obtained from integrating the ac current, as

$$q = \frac{I_0 \exp(j(\omega t + \phi))}{j\omega Z_e} = \frac{E_0 \exp(j\omega t)}{j\omega Z_e}$$  \[5\]

We can then define a general stress-charge coefficient, $\zeta$, mentioned in the introduction as,

$$\zeta = \frac{dF}{dq} = \frac{j\omega Z_e}{E_0 \exp(j\omega t)} = j\omega Y_e Z_e$$  \[6\]

that can be obtained from experimental values of the electrochemical impedance and the stress admittance. We have used this method to examine the potential dependency of $\zeta$ for both Au and Pt cantilever electrodes in HClO$_4$ electrolyte, at potentials ranging from hydrogen evolution to oxide formation.$^{34,35}$

In a typical D.S.A analysis of Cu deposition, the potential of the Au cantilever electrode was stepped from the open circuit potential to the desired deposition potential while the current, potential, and $F$ were recorded simultaneously as functions of time. The current was integrated to determine the deposit thickness. After the deposit thickness exceeded 100 nm, the ac signal was superimposed to the steady-state deposition potential to begin the D.S.A measurement. D.S.A was performed in the thickness range of 100 nm to 800 nm. The ac component of the D.S.A output signals were analyzed by the Levenberg-Marquardt algorithm$^{38}$ in order to determine the frequency, amplitude and phase shift that best fit the experimental data. The variance of each parameter was determined from the diagonal of the covariance matrix and is reported as a standard deviation in the form of error bars. If the detected fundamental frequency of either the current or $F$ did not match the input frequency of the potential, the data set at that frequency was discarded. Steady state deposition potentials ranging from −0.48 V to −0.57 V were examined. More positive potentials were avoided in order to ensure that the potential never exceeded the Cu rest potential of −0.41 V during the D.S.A measurements, thus avoiding Cu dissolution. A minimum of 20 frequencies was typically examined, in the range of 0.1 Hz to 20 Hz. The upper frequency is limited by the resonant frequency of the cantilever, which for the cantilever used in this study is about 40 Hz.$^{34}$ This serves as a maximum frequency for D.S.A measurements since the cantilever response close to resonance depends overwhelmingly on its mechanical properties and the effects of electrochemistry become negligible. Voltage amplitudes ranging from 20 mV to 40 mV were applied. We recognize that 40 mV is a much larger amplitude than is typically used in EIS. Such large amplitudes are sometimes necessary in order to generate a measurable stress signal. In our previous work on Au$^{39}$ and Pt$^{40}$ we determined that both the current and stress behaved linearly for amplitudes as high as 80 mV at potentials in the double layer region. We have not determined the extent of the linear region for Cu deposition. However, we have observed that although the total harmonic distortion (THD) of the response signals increases slightly with increased amplitude, the stress response, when normalized to the charge, is very similar.
was tensile (i.e., > 0). The compressive stress often observed in the pre-coalescence regime of Volmer-Weber film growth was not apparent in these stress-thickness curves. This is in part due to the underpotential deposition (upd) of Cu onto Au. This early transition to tensile stress has been attributed to Cu nano-crystallites, nucleated at Au defects and step edges, that start to coalesce after just one or two monolayers of bulk Cu have been deposited.\(^{36,40}\) A small compressive region has been observed for Cu films electrodeposited from dilute (10 mmol/L) CuSO\(_4\) electrolyte.\(^{36}\) The stress-thickness curves in Fig. 2 reach a constant slope after about 250 nm of Cu was deposited. If it can be assumed that the stress in previously deposited Cu does not relax during deposition then the slope along any point of these curves corresponds to the incremental or instantaneous stress; i.e., the in-plane stress of new Cu being deposited at the surface where \(z = h_f\). We will refer to the linear region where the incremental stress is constant as the steady-state stress, \(\sigma_{ss}\) where

\[
\sigma_{ss} = \sigma(h_f) = \frac{d(\partial h_f)}{dh}
\]

for values of \(h_f\) where the slope \(d(\partial h_f)/dh\) is constant. If we evaluate the slope in the thickness range of 500 nm to 600 nm, the steady-state stress values range from 36 MPa to 85 MPa and increase as the deposition potential is made more negative. This is consistent with current stress generating models that predict increasingly tensile growth stress as the growth rate is increased.\(^{25}\) Figure 2 also shows the stress-thickness for a 3-minute period following deposition where the Cu deposit is allowed to rest at the open-circuit potential. Little stress relaxation is observed at low to moderate overpotentials whereas relaxation of tensile stress is seen for large overpotentials. Although the relaxation of tensile stress is not extensively discussed in the literature, it is generally attributed to the reduction of coalescence-induced strain energy by surface diffusion.\(^{22}\) The fact that we do not observe relaxation of compressive stress following deposition suggests that the reversible diffusion of adatoms into grain boundaries is not a prominent stress generating mechanism for Cu under these deposition conditions.

We now examine stress generation with DSA. Figure 3 shows a plot of stress-thickness vs. thickness for Cu deposition at \(-0.55\) V, with and without the DSA signal applied to the deposition potential. In this case, the applied DSA signal (also plotted in Fig. 3) was 40 mV over a frequency range of 0.1 Hz to 20 Hz. The DSA signal was initiated after the deposit thickness reached 140 nm, with the high frequency applied first. Although the cantilever clearly responds to the DSA input (note the small oscillations in the stress-thickness at low frequency), the overall stress response is not seriously altered by the application of the DSA signal and both curves indicate a steady-state stress of about

![Figure 1](https://example.com/figure1.png)  
**Figure 1.** Chronoamperometry response for Cu electrodeposition onto Au cantilever electrodes in 1.8 mol/L H\(_2\)SO\(_4\) containing 0.1 mol/L CuSO\(_4\). The potential was stepped from \(+0.1\) V vs SSE to deposition potentials ranging from \(-0.48\) V to \(-0.60\) V for a total deposit thickness of 600 nm. The inset is the linear sweep voltammetry (5 mV/s sweep rate) showing the range of potentials examined in relation to the diffusion-limited current.

We conclude that although linearity may not be maintained, the phase and amplitude of the fundamental frequency are not seriously altered.

**Results**

**Steady-state stress.**—Figure 1 shows the current response for 600 nm Cu films, electrodeposited at potentials ranging from \(-0.48\) V to \(-0.60\) V, in the absence of DSA. For all potentials examined, the current density relaxed to a steady-state value within about 65 s, the value of which increased as the deposition potential was made more negative. This is a clear indication that the diffusion-limited current had not been reached and that Cu deposition was under mixed kinetic-diffusion control over this range of deposition potentials. The steady-state deposition currents ranged from 4.6 to 10.7 mA/cm\(^2\). The inset in the figure shows the linear sweep voltammetry (5 mV/s sweep rate) in the same solution, indicating the range of potentials examined in relation to the potential at which Cu deposition becomes diffusion-limited.

Figure 2 shows the corresponding stress-thickness curves for the chronoamperograms shown in Fig. 1. In all cases the stress-thickness

![Figure 2](https://example.com/figure2.png)  
**Figure 2.** Evolution of stress-thickness product vs. deposit thickness associated with the chronoamperometry curves shown in Fig. 1. The stress-thickness is also shown for a 3-minute period at open circuit following deposition in order to monitor stress relaxation.
+60 MPa. Ideally, the DSA signal should be initiated once the stress reaches steady-state. However, in order to apply the same frequency range for all deposition potentials, the DSA signal had to be initiated early for the more negative deposition potentials, such as that shown in Fig. 3. The consequences of this will be discussed later.

**DSA: stress vs. time response.**—Figure 4 shows a typical stress response to a steady-state deposition potential of −0.52 V and DSA input voltage of 40 mV at frequencies of 5.3 Hz (a) and 0.13 Hz (b). Only the ac component of the stress is shown; the dc component has been removed for clarity. In both cases, the stress oscillates at the same frequency as the input voltage; however, their amplitude and phase angle vary significantly. The stress response at 5.3 Hz in (a) has an amplitude of about 0.02 N/m and is 180° out of phase with respect to the voltage. In contrast, the stress response at 0.13 Hz in (b) has a significantly larger amplitude of 0.15 N/m and is phase-shifted to the right (smaller phase angle). In addition, small distortions appear in the stress response that suggest higher harmonics have been introduced, an indication that the system is not behaving linearly.

**DSA: frequency dependency.**—We now take a more detailed look at the stress response as a function of frequency. Figure 5a is a plot showing the magnitude of the stress admittance \( Y_{s,0} \) over a frequency range of 0.1 Hz to 25 Hz for a variety of Cu deposition potentials. At high frequency, all of the admittance values converge to the same value of about 0.65 N/(V·m). As the frequency decreases, the admittance increases; i.e., the stress response for a given \( E_0 \) increases. The frequency at which this increase occurs is a function of the deposition potential. Figure 5a also shows the response of a Cu cantilever in \( Cu^{2+} \)-free electrolyte at −0.55 V. The stress response matches that for Cu deposition at high frequency, but does not show the admittance increase as the frequency is reduced.

Similar behavior is seen in the phase angle of the stress (\( \phi_s \)), shown in Fig. 5b. At high frequency, all curves converge to a value approaching 180°; i.e., the stress and the applied potential are perfectly out of phase. As the frequency decreases, the phase angle decreases for those cantilevers undergoing Cu deposition while the control cantilever remains 180° out of phase. Although the potential dependency of the Fig. 5b phase angle decrease is nearly as clear as the magnitude of the stress admittance, it is apparent that the phase angle begins to decrease at higher frequency for the more negative deposition potentials. This phase angle decrease seen for Cu deposition is the same negative phase shift seen in the stress-time curves plotted in Fig. 4. Whereas the stress response is 180° out of phase with the potential at a frequency of 5.3 Hz, it shifts to the right (less positive) at the lower frequency.

The frequency dependency of the stress response in Fig. 5 indicates that over the frequency range examined, at least two stress-generating processes are evident. The fact that both the admittance and phase angle values at high frequency are independent of the potential of \( Cu^{2+} \) in solution suggests that this stress response is due to double layer charging. Although the electrocapillary behavior of Cu has yet to be reported, this behavior is consistent with recent electrocapillary studies performed on Au34 and Pt35 in HClO4 electrolyte in the double layer region where the stress and potential were also found to be close to 180° out of phase over a wide frequency range.

**Electrochemical impedance.**—In an effort to identify the possible stress contributions as well as their frequency dependency, we examine the electrochemical impedance for Cu electrodeposition onto the Au cantilever electrodes. A 100 nm thick film of Cu was electrodeposited onto the Au prior to starting the impedance measurements. The stress was not measured so that higher frequencies could be assessed. Figure 6a shows the Nyquist plots (imaginary Z′ vs real Z′′) for various deposition potentials over a frequency range of 0.1 Hz to 10 kHz. The characteristic feature of the impedance is a depressed
Figure 5. (a) The magnitude of the stress admittance, $Y_{sd}$, as defined by Eqn. 4 and (b) the phase angle of the stress, $\phi_s$, as a function of applied frequency for Cu deposition at the potentials shown in the figure. The electrolyte was 0.1 mol/L CuSO$_4$ in 1.8 mol/L H$_2$SO$_4$ and the amplitude of the DSA signal was 40 mV. Also shown are the admittance and phase angle of a Cu cantilever electrode at $E_{dc}$ of $-0.55$ V with no Cu$^{2+}$ present in solution.

Figure 6. (a) Nyquist plots (imaginary $-Z''_e$ vs real $Z'_e$) of the electrochemical impedance of a Cu cantilever electrode in 0.1 mol/L CuSO$_4$ in 1.8 mol/L H$_2$SO$_4$ for various deposition potentials over a frequency range of 0.1 Hz to 10 kHz and applied amplitude of 35 mV. The solid lines represent a fit to the equivalent circuit shown in (b). The fit results are listed in Table I. The listed frequencies are for the $-0.50$ V data.

Table I. Fit results of the electrochemical impedance data shown in Fig. 6a to the equivalent circuit shown in Fig. 6b.

| Potential (V) | $R_s$ ($\Omega$-cm$^2$) | $Y_{dl}$ ($\mu$S-s$^{-1}$/cm$^2$)$^*$ | n | $R_{ct}$ ($\Omega$-cm$^2$) | $Y_w$ (S$^{-1/2}$/cm$^2$)** | $C_{dl}$ ($\mu$F/cm$^2$)$^***$ |
|--------------|----------------|----------------------------------|---|----------------|----------------|----------------|
| $-0.48$      | 0.72           | 503.3                            | 0.70 | 13.2         | 0.92           | 57.90       |
| $-0.50$      | 0.78           | 268.3                            | 0.77 | 12.6         | 0.98           | 48.55       |
| $-0.52$      | 0.90           | 188.3                            | 0.81 | 10.8         | 1.00           | 43.96       |
| $-0.55$      | 0.96           | 178.3                            | 0.83 | 8.4          | 0.62           | 47.47       |
| $-0.57$      | 0.90           | 255.0                            | 0.80 | 8.4          | 0.47           | 55.43       |
| $-0.60$      | 0.96           | 260.0                            | 0.82 | 7.2          | 0.30           | 65.51       |

$^*$The admittance of the constant phase element CPE$_{dl}$ is equal to $Y_{dl}(j\omega)^n$.

$^{**}$The admittance of the Warburg element W is equal to $Y_w(j\omega)^{1/2}$. Since the measurements did not extend too far into the low frequency regime, the Warburg impedance does not need to be represented by the hyperbolic tangent formula.

$^{***}$The effective double layer capacitance $C_{dl}$ was calculated from $Y_{dl}$.41,44

For the case of Cu deposition that can be represented by the equivalent circuit in Fig. 6b, this force is comprised of two parts, the force due to electrocapillarity (double layer charging) and the mechanical response of the cantilever is due to the force (per unit area) exerted on the cantilever as a result of electrochemical processes taking place on the cantilever electrode surface. For the case of Cu deposition that can be represented by the equivalent circuit in Fig. 6b, this force is comprised of two parts, the force due to electrocapillarity (double layer charging) and the mechanical response of the cantilever is due to the force (per unit area) exerted on the cantilever as a result of electrochemical processes taking place on the cantilever electrode surface. For the case of Cu deposition that can be represented by the equivalent circuit in Fig. 6b, this force is comprised of two parts, the force due to electrocapillarity (double layer charging) and the
force due to metal deposition. The stress response associated with each branch will depend on the amount of charge partitioned through each branch, based on its impedance, as well as the stress-charge coefficient associated with each process, and can be described by the general expression shown in Eqn. 6. Since the stress admittance for these parallel processes is additive, the overall stress admittance can be expressed as

$$Y_s = Y_{s, dl} + Y_{s, f} = \frac{\zeta_{dl}}{j\omega C_{dl}} + \frac{\zeta_f}{j\omega Z_f} \quad [8]$$

where we define a separate stress admittance ($Y_{s, dl}$, $Y_{s, f}$), stress-charge coefficient ($\zeta_{dl}$, $\zeta_f$), and electrochemical impedance ($Z_{dl}$, $Z_f$) for the double layer and faradaic branches, respectively. Equation 8 indicates that the overall stress response ($Y_s$) can be calculated from the measured electrochemical impedance ($Z_{dl}$ and $Z_f$), with knowledge of the stress-charge coefficients ($\zeta_{dl}$ and $\zeta_f$) for the separate capacitive and faradaic branches of the equivalent circuit. For the equivalent circuit shown in Fig. 6b, we can define $Z_{dl}$ and $Z_f$ as,

$$Z_{dl} = \frac{1}{\text{Y}_{dl}(j\omega)^n} \approx -\frac{j}{\omega C_{dl}} \quad [9a]$$

$$Z_f = R_f + Z_w = R_{f} + \frac{1}{\text{Y}_{f}\sqrt{j\omega}} \quad [9b]$$

where $C_{dl}$ is the effective double layer capacitance calculated from the constant phase element (CPE$_{dl}$). $Z_w$ is the Warburg impedance, and $Y_w$ is the Warburg coefficient. Since the measurements did not extend too far into the low frequency regime, $Z_w$ does not need to be represented by the hyperbolic tangent formula.

We can make use of the stress data in Fig. 5 for the Cu cantilever in Cu$_2^+$-free electrolyte. Since there is no stress contribution from Cu deposition, the faradaic term in Eqn. 8 is zero, such that

$$\zeta_{dl} = Y_{s, dl}$$

The Cu$_2^+$-free $Y_{dl}$ data plotted in Fig. 5 exhibited no frequency dependency, as expected for double layer charging. We can use make use of the electrochemical impedance data from the same Cu$_2^+$-free control experiment; the Nyquist plot is shown in Fig. 7a. Although Cu$_2^+$ was not present in solution, there was still a measurable faradaic current at $-0.55$ V, presumably the reduction of O$_2$ that remained entrained in the electrolyte. The steady-state current density was less than 10 $\mu$A/cm$^2$ which is consistent with O$_2$ reduction from Ar-purged electrolyte. We treat this parasitic reaction as a non-stress generating, diffusion-limited faradaic process and fit the data to the equivalent circuit shown in Fig. 6b; however we replace the constant phase element CPE$_{dl}$ with a capacitance $C_{dl}$ since the constant phase element is not required to adequately fit the data. The solid line is a fit of the data while the best-fit parameters are listed in the Fig. 7a plot. The impedance of the capacitive branch is then $Z_{dl} = -j\omega C_{dl}$ and can be calculated from $C_{dl}$ obtained from the fit. With $Y_{dl}$ and $Z_{dl}$ in hand, we can now calculate $\zeta_{dl}$ from Eqn. 8. Since $C_{dl}$ is a complex variable, it can be represented by its magnitude ($C_{dl}$,$\theta$) and phase angle, as shown in Fig. 7b. Recall that $\zeta_{dl}$ is the stress-charge coefficient, with units of Nm/C or simply V. It quantifies the force due to metal deposition. The stress response associated with each branch will depend on the amount of charge partitioned through each branch, based on its impedance, as well as the stress-charge coefficient associated with each process, and can be described by the general expression shown in Eqn. 6. Since the stress admittance for these parallel processes is additive, the overall stress admittance can be expressed as

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We now examine the stress-charge coefficient for Cu deposition, $\zeta_f$. The time derivative of the stress-thickness response for Cu deposition can be expressed as

$$\frac{d(\bar{\sigma}h_f)}{dt} = \frac{d\bar{\sigma}}{dt}h_f + \sigma(h_f) \frac{dh_f}{dt} \quad [11]$$

The first term on the right side captures any relaxation processes that might occur in material that has already been deposited, while the second term corresponds to changes in the film thickness with stress $\sigma(h_f)$. Although we expect that DSA will serve as an excellent technique for characterizing reversible stress relaxation processes (for instance adatom diffusion into grain boundaries), the open circuit stress data in Fig. 2 indicates that under the deposition conditions examined here and at low to moderate overpotentials, stress relaxation will be a small component of the DSA stress response. Equation 11 then simplifies to

$$\frac{d(\bar{\sigma}h_f)}{dt} \approx \sigma(h_f) \frac{dh_f}{dt} = \sigma_{ss} \frac{dh_f}{dt} \quad [12]$$

where $\sigma(h)$ is replaced by $\sigma_{ss}$ since DSA is applied in the linear region of the stress-thickness curve. The change in thickness can be equated to charge ($q$), through Faraday’s law

$$dh_f = -q F_{Farad} n p \quad [13]$$

where $F_{Farad}$ is the Faraday constant, and $M$, $p$, and $n$ are the molar mass, density, and number of equivalents, respectively for Cu. This
leads to the following expression
\[
\frac{d(\delta h_f)}{dq} = \zeta_f = -\alpha_{st} \frac{M}{F_{ju} n \rho}
\]  
[14]

which simply states that the stress-charge coefficient for Cu deposition is proportional to the value of the steady-state stress. For example, using a stress of +60.9 MPa that was measured for the −0.55 V deposit (Fig. 3), one obtains a value for \( \zeta_f \) that is equal to \(-2.3 \times 10^{-3}\) V, or roughly 400 times smaller than \( \zeta_{dl} \). There are a couple of obvious points to be made regarding this result. The first is that the calculated value of \( \zeta_f \) is negative, similar to \( \zeta_{dl} \). This simply reflects the fact that negative charge causes a positive change in the stress-thickness since the Cu that is added to the deposit is under tensile stress. The second obvious point is that \( \zeta_{dl} \) is nearly three orders of magnitude larger than \( \zeta_f \). This simply reflects the large forces associated with surface stress. Surface stresses arise because the configuration of atoms at a surface is different from that in the bulk, the interior atoms exerting a stress on the surface atoms that forces them to adopt the bulk crystal configuration, at least biaxially in the plane of the surface. Cu (111) is reported to have a surface stress of +0.86 N/m. The equivalent bulk stress, assuming a surface monolayer thickness of 0.21 nm, is about 4 GPa, or about 75 times larger than the stress measured in the Cu deposits.

With knowledge of the stress-charge coefficients, we can now use Eqn. 8 to calculate the stress response from the electrochemical impedance \( Z_{dl} \) and \( Z_f \) that were obtained from the equivalent circuit elements listed in Table I. The stress simulations are shown in Fig. 8, where the magnitude of the stress admittance \( Y_{s,0} \) and the phase angle \( \phi \) are plotted as a function of frequency. Both parameters are similar to the experimental data shown in Fig. 5 with respect to magnitude as well as the frequency and potential dependency. At high frequency, \( Y_{s,0} \) and \( \phi \) converge to values of about 0.4 N/(Vm) and 180°, respectively. This frequency region is controlled by electrocapillarity. The slight variation in \( Y_{s,0} \) with potential at high frequency is due to the potential dependency of \( C_d \) (Table I). The Cu growth stress contribution is small at high frequency due to the small change in deposit thickness (charge) associated with the voltage perturbation as well as the extremely low value of the stress-charge coefficient \( \zeta_f \). As the frequency is decreased, the stress admittance response can be traced to the charge associated with each branch of the equivalent circuit (not shown). For the capacitive branch the charge is constant so the electrocapillarity contribution remains constant as well. In contrast the charge associated with Cu deposition increases by a factor of nearly 200 as the frequency is decreased from 25 Hz to 0.1 Hz for the −0.57 V deposit. This significant increase in charge makes the growth stress contribution relevant at low frequency, in spite of the low value of \( \zeta_f \). Since the growth stress of the deposit contributes little to the overall stress response at high frequency, our decision to initiate the DSA signal before the stress reaches steady-state (see Fig. 3) has little consequence.

These competing processes are also responsible for the frequency dependency of the phase angle. Figure 9 is a schematic showing the expected phase angles for various parameters for the two cases where one of the two branches (electrocapillarity or Cu deposition) dominates. Our reference state is the input voltage signal, which defines our zero phase angle. The red box in the schematic represents the case where double layer charging dominates the stress response. Since this branch behaves as a simple capacitor, the current is +90° phase shifted from the potential while the charge is in-phase with the potential. Since the stress-charge coefficient \( \zeta_{dl} \) is negative, the stress is phase-shifted 180° from both the potential and charge. This is what is observed at high frequency in both the simulations (Fig. 8b) and experimental data (Fig. 5b). This is also the phase angle observed at all frequencies of the Cu²⁺-free data where only double layer charging occurs. The blue box in the schematic represents the case where the Faradaic branch, Cu deposition, dominates the stress response. In the absence of appreciable Warburg impedance, the Faradaic current is in-phase with the potential so the charge is shifted −90°. Since \( \zeta_f \) is also negative (negative charge results in tensile stress), the stress is

![Figure 8](https://example.com/fig8.png)

**Figure 8.** Calculated (a) stress admittance \( Y_{s,0} \) and (b) phase angle \( \phi \) using Eqn. 8. \( Z_{dl} \) and \( Z_f \) were calculated from the equivalent circuit elements in Table I. \( \zeta_f \) was calculated from Eqn. 14 using the steady-state stress obtained from the slope of the stress-thickness vs. thickness curve (as in Fig. 3), and \( \zeta_{dl} \) was calculated from Eqn. 10, using Cu²⁺-free stress data, and assumed to have a constant value of −0.91 V for all deposition potentials.

![Figure 9](https://example.com/fig9.png)

**Figure 9.** Schematic showing the expected phase angles for current density, charge density, and stress for the two limiting cases where one of the two branches, electrocapillarity (red box) or Cu deposition (blue box) dominates the stress response. The continuous blue box and the dashed blue box show the expected phase angle of the deposit stress when the steady-state stress of the Cu is tensile (\( \sigma^+ \)) and compressive (\( \sigma^- \)), respectively. Note that −180° and +180° are equivalent.
phase shifted 180° from the charge, giving it a phase of +90° with respect to the input potential. As the stress generating process proceeds from electrocapillarity at high frequency to Cu deposition at low frequency, the phase angle of the stress is expected to decrease from +180° to +90°, as seen in both the simulations and the experimental data.

The simulated stress curves shown in Fig. 8 suggest that the experimental stress response can be explained by considering two sources of stress, electrocapillarity and deposit growth stress. The relative contributions of each can be determined from the equivalent circuit that describes the electrochemical impedance. Since these stress-generating mechanisms have dramatically different frequency dependency, Cu deposition is a nice demonstration that highlights the attributes of DSA: i.e., using frequency to separate the various stress contributions. It also clearly demonstrates that similar to electrochemical impedance, DSA measurements can be made far from equilibrium, during steady-state electrodeposition. The steady-state response can be ignored and we can focus only on the electrode/cantilever response to the small, superimposed ac signal. The potential dependency is captured by the change in the equivalent circuit elements (Table 1) and the deposit steady-state stress with overpotential. In addition, the small ac signal does not alter the steady-state response, as clearly shown in Fig. 3. It is also worth noting that the DSA signal can be applied in any number of ways. Here we examine the frequency dependency during steady-state Cu deposition. However a single frequency (or small range of frequencies) can be applied at the onset of deposition to examine the reversible stress response during nucleation, coalescence, and growth.

With our current understanding, we can also predict the expected stress response for other stress situations, such as Cu deposition at low growth rate or from dilute solution where the steady-state stress is reported to be compressive.25,36 In this case the electrocapillary stress relaxes at positive potential (or small angle shift that provides the fundamental information about the active stress components.

Although no stress relaxation was required to adequately simulate the experimental data for the Cu deposition conditions examined here, DSA should serve as an excellent technique for characterizing reversible stress relaxation processes. In principle stress relaxation can be treated as an additional stress-generating branch on the equivalent circuit. For example, under deposition conditions where the reversible diffusion of adatoms into grain boundaries is a stress generating mechanism, then potential modulation could alter the chemical potential of adatoms at the surface and as a consequence, their flux into and out of the grain boundaries. In addition to electrocapillarity and growth stress, one would expect a modulation in the stress specifically due to diffusion of adatoms into grain boundaries is a stress generating mechanism. This process would then have a phase angle shift that provides the fundamental information about the active stress components.

Conclusions

Stress development during the electrodeposition of copper was analyzed by dynamic stress analysis (DSA), an in situ characterization technique that combines electrochemical impedance spectroscopy (EIS) with cantilever curvature. Under the deposition conditions examined here, the steady-state stress that develops after deposition of 500 nm of Cu is tensile, ranging from 36 MPa to 85 MPa, and increasing with deposition overpotential. Two sources of stress can account for the dynamic stress behavior in the frequency range of 0.1 Hz to 25 Hz. The high frequency region is controlled by electrocapillarity (double layer charging); the amplitude of the stress response is rather small and is 180° out of phase with respect to the input potential. Low frequency is dominated by the growth stress of the Cu film. The amplitude of the stress response increases with decreasing frequency and its phase angle shifts to +90°. Both of these transitions are potential dependent and can be modeled from the electrochemical impedance, making use of separate stress-charge coefficients for double layer charging and Cu deposition.

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