The Effects of Plating Current, Grain Size, and Electrolyte on Stress Evolution in Electrodeposited Ni

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Measurements were performed to study the influence of growth rate (plating current), grain size, and electrolyte concentration on stress evolution in Ni electrodeposited from an additive-free Ni sulfamate bath. The stress measurements were conducted by the wafer curvature method during electroplating, and the corresponding grain sizes were determined post-deposition from cross-sections made using a Focused-Ion Beam (FIB). The results were interpreted using a kinetic model which focuses on the incremental stress generated at the triple junction where adjacent islands impinge upon each other. The stress vs. growth rate does not change significantly when the Ni sulfamate concentration was changed at fixed boric acid concentration, but it did change when the boric acid concentration was altered. This is discussed in terms of the effect of the electrolyte concentration on the exchange current and interfacial energy.

Thin films have long played a critical role in microelectronic interconnects. Consequently, residual stress in thin films has long been a problem since it can adversely affect the performance and reliability of devices. Residual stress refers to the stress that is induced by growth of the material, apart from external factors such as thermal expansion mismatch. Determining the relationship between the stress and the processing conditions is key to controlling it. Furthermore, a fundamental understanding of the underlying mechanisms that produce residual stress allows the stress to be tailored and predicted.

There have been many studies of stress evolution and some general trends with the processing conditions and material have been observed. Abermann classified stress behavior into two types based on measurements of evaporated films. For materials with high melting point or low mobility (type I), tensile stress develops during the coalescence stage, and does not change significantly with further film growth. For materials with low melting point or high mobility (type II), the stress is tensile in the coalescence stage but becomes compressive as the film thickness increases. When the growth flux is turned off, the stress in type I materials generally does not change but type II materials exhibit significant relaxation. Changing the growth rate or deposition temperature can also alter the stress evolution behavior. The general understanding is that the stress is more likely to be tensile at low atomic mobility, low temperature, or high growth rate while the stress is more compressive or less tensile for high atomic mobility, high temperature, or low growth rate.

Microstructural evolution in thin films can also significantly affect the stress evolution. Depending on the material and processing conditions, the grain size can remain constant, change primarily at the surface grain growth or grain growth can occur throughout the film. This can change the film stress by affecting the stress at the surface as new layers are deposited or by inducing stress through grain growth in the previously-deposited layers.

In the current study, we used electrodeposition in an additive-free sulfamate-based bath to obtain the Ni films. We investigate the effect of growth rate (plating current), grain size and electrolyte concentration on the stress evolution. Because these effects can be coupled, we perform systematic measurements to understand the effect of these parameters individually. This is done by measuring the stress vs. growth rate for different concentrations and subsequently cross-sectioning the sample to characterize the grain size that corresponds with each measurement. The data are interpreted in terms of a kinetic model discussed in Kinetic model for steady-state stress during growth sections that describes the dependence of the stress on growth rate (R), effective diffusivity (D) and grain size (L). It has been used in previous studies of electrodeposited Cu and Ni to interpret the effect of growth rate and grain size on stress.

There have only been limited studies reporting the effect of Ni sulfamate concentration or boric acid concentration on in-situ stress evolution in Ni plated from additive free sulfamate baths. In that work, plating efficiency was observed to be a factor influencing stress during electrodeposition from Ni sulfamate baths. It was observed that the onset of hydrogen evolution at plating efficiencies below 97% induced tensile intrinsic stress in Ni electroplated from high-speed Ni sulfamate baths. The work also linked a local rise in pH at the plating surface with tensile stress generation. However, the microstructural source of the tensile stress was not identified. In addition, hydrogen in Ni electroplated from Ni sulfamate baths has also been linked to compressive stress generation. This work found that presence of atomic hydrogen at a Ni surface induced a small reversible compressive stress. It was the assertion of that work that the observed stress from hydrogen was the result of atomic hydrogen inserting into the Ni lattice during plating and then diffusing out when plating was stopped. Previous research has also reported that the addition of saccharin to the electrolyte refines the microstructure in Ni films. The role of hydrogen, plating efficiency and other additives was deemed to be outside the scope of this work, but represents an interesting opportunity for additional study.

Experimental

The samples were initially prepared by evaporating 5 nm Ti and 150 nm Au onto a (100) Si substrate with dimensions of 25 mm × 10 mm × 0.2 mm. The Ti layer was deposited onto the Si as an adhesion layer for Au layer, and the Au layer worked as a conductive seed layer for the Ni electrodeposition. Ni films were electrodeposited at room temperature under galvanostatic control using a saturated calomel (SCE) reference electrode. The first 1 μm Ni layer was electrodeposited as a buffer layer to ensure that the films had similar microstructures after the coalescence regime. The experiments were conducted with two sets of electrolyte concentrations. The first set of electrolytes were prepared by keeping the concentration of boric acid constant at 0.65 mol/L and...
then varying the concentration of Ni sulfamate at 0.18 mol/L, 0.36 mol/L, or 0.50 mol/L; the second set of electrolytes were prepared by keeping the concentration of Ni sulfamate constant at 0.36 mol/L and then changing the concentration of boric acid from 0.18 mol/L to 0.65 mol/L. Before electrodeposition, the electrolyte solutions were bubbled through Nitrogen gas (N2) for 1 hour to reduce the content of oxygen in the solution. After deposition, samples were rinsed with DI (de-ionized) water and dried with compressed N2 gas.

Table I shows the measured plating efficiency for the baths used in this work. The ideal growth rate is calculated using Faraday’s law by assuming that the efficiency is equal to 1. The plating efficiency is calculated from the ratio between the actual growth rate, measured by FIB cross-sectional micrographs, and the ideal growth rate. This data shows a significant decrease in plating efficiency at the highest plating rates and lowest boric acid concentrations. The data is consistent with past literature observations where it was observed that Ni sulfamate concentration having little impact on the measured plating rate and efficiency, whereas boric acid concentrations in solution have a much stronger impact on the plating efficiency.16,19

The stress evolution during deposition was measured by Multi-beam Optical Stress Sensor (MOSS). This method enables us to monitor the curvature changes during film deposition. The average stress (\(\overline{\sigma}\)) in the film is related to the curvature (\(\kappa\)) by Stoney’s equation:20

\[
\kappa = \frac{6\overline{\sigma}h_f}{M_f h_s^2} \quad [1]
\]

where \(h_f\) is the film thickness, \(h_s\) is the substrate thickness, and \(M_f\) is the biaxial modulus of the substrate. \(\overline{\sigma}\) is referred to as stress-thickness; it can be calculated by integrating the in-plane stress distribution over the thickness of the film:

\[
\overline{\sigma}h_f = \int_0^{h_f} \sigma(z,t) \, dz \quad [2]
\]

A single curvature measurement only gives the average stress at a single film thickness. However, if the stress is not uniform throughout the film thickness, we should also consider the stress evolution with time. The stress distribution can thus be calculated by the time derivative of stress-thickness:

\[
\frac{d\overline{\sigma}(h_f)}{dt} = \frac{d(h_f)}{dt} \kappa + \int_0^{h_f} \frac{\partial \sigma(z,t)}{\partial t} \, dz \quad [3]
\]

The first term on the right represents the effect of stress changes as a result of the addition of a new layer onto the surface of the film at a rate of \(d(h_f)/dt\). \(\overline{\sigma}(h_f)\) is referred to as incremental stress or instantaneous stress. The second term represents the effect of stress changes in the layer that has been deposited. If the stress in the existing layer does not change after deposition (i.e., \(\partial \sigma(z,t)/\partial t = 0\)), then the incremental stress can be obtained by measuring the slope of stress-thickness versus film thickness:

\[
\sigma(h_f) = \frac{d\overline{\sigma}(h_f)}{dh_f} / \frac{d(h_f)}{dt} \propto \frac{dk}{dh_f} \quad [4]
\]

Note that this equation is only applicable when the film thickness is much smaller than that of the substrate. When the film thickness is large, as is the case in this study, a correction of this equation21 can be used to relate the slope of the curvature measurement to the incremental stress in the film:

\[
\sigma(h_f) = \left\{ \frac{(M_s h_s^3 + M_f h_f^3)(M_s h_s^3 + M_f h_f^3)(M_s h_s^3 + M_f h_f^3)}{3} - \frac{(M_s h_s^3 - M_f h_f^3)^2}{4} \right\} \frac{dk}{dh_f} \quad [5]
\]

where \(M_f\) is the biaxial modulus of the film material.

The grain size was measured using scanning electron microscopy (SEM) on FIB cross-sections of the sample. An intercept method was employed as described in ASTM standard E112-1222 to estimate the average grain size at different depths in the film. The method includes a geometric correction that assumes the grains are circular. The average and standard deviation of the grain size were determined by analyzing multiple grains in 5–7 micrographs taken at different places in the sample. The grain size was not determined for film thicknesses less than 1 \(\mu m\).

There are some desired grain sizes for film growth. The results of the study can be verified by using these grain sizes for film growth. The stress-thickness evolution is therefore similar for the first micron of each data set. When the growth rate is changed, the slope changes to a new value. The slope is larger for larger growth rates, indicating that the incremental stress becomes more tensile with increasing growth rates. Conversely, the stress is more compressive or less tensile for lower growth rates. This is consistent with previous studies on electrodeposited Ni.7,14,16,23

| Current density (mA/cm²) | Ideal growth rate (mm/s) | 0.18 Ni 0.36 acid | 0.36 Ni 0.65 acid | 0.50 Ni 0.65 acid | 0.36 Ni 0.18 acid |
|--------------------------|--------------------------|-------------------|------------------|------------------|------------------|
| 0.322                    | 0.11                     | N/A               | N/A              | N/A              | 0.85             |
| 0.644                    | 0.22                     | 0.96              | 0.96             | 0.95             | 0.90             |
| 1.292                    | 0.44                     | 0.95              | 0.96             | 0.94             | 0.87             |
| 5.378                    | 1.84                     | 0.91              | 0.94             | 0.91             | 0.85             |
| 10.763                   | 5.67                     | 0.87              | 0.90             | 0.88             | 0.82             |
| 21.516                   | 7.35                     | 0.73              | 0.83             | 0.83             | 0.75             |
| 32.276                   | 11.02                    | 0.63              | 0.72             | 0.73             | 0.68             |

The stress-thickness evolution was measured in several ways; during continuous growth at one growth rate, with periodic pauses during growth at one rate and for intervals of growth at different rates with pauses between them. As described below, these different strategies enable the effects of relaxation and grain growth on the stress to be determined.

Measurements of stress-thickness vs. thickness for continuous growth of Ni films is shown in Figure 1. The films were galvano-statically electrodeposited at room temperature from an electrolyte of 0.36 mol/L Ni sulfamate and 0.65 mol/L boric acid. In each case, the first 1 \(\mu m\) of the Ni film was deposited at a growth rate of 3.30 nm/s. This was used as a uniform buffer layer to ensure similar grain size and morphology when subsequent growth at new rates was started. The stress-thickness evolution is therefore similar for the first micron of each data set. When the growth rate is changed, the slope changes to a new value. The slope is larger for larger growth rates, indicating that the incremental stress becomes more tensile with increasing growth rates. Conversely, the stress is more compressive or less tensile for lower growth rates. This is consistent with previous studies on electrodeposited Ni.7,14,16,23
The evolution of stress-thickness vs. thickness at a single growth rate of 3.30 nm/s with periodic pauses is shown in Figure 2. The vertical dashed lines correspond to the periods when the growth rate was interrupted and the thickness was constant. The data indicates that the slope of the stress-thickness is the same when the growth is resumed as it was before the growth was terminated. The curve is also continuous after the pauses, showing that the stress did not relax when the growth was turned off and attains the same value when the growth is turned back on. The time evolution of the stress-thickness including the pauses is shown in the inset of the figure. The shaded areas correspond to periods when the deposition is turned off. It can clearly be seen that the stress-thickness does not change significantly during the pauses.

This behavior indicates that the stress in the deposited layers does not relax measurably when the growth is turned off. It also suggests that the grain size does not change significantly during the pauses. This is quite different from electrodeposited Cu and electrodeposited Sn. In electrodeposited Sn, the stress-thickness change is reversible (i.e., the stress-thickness relaxes when the growth flux is turned off, but returns to the same value when the growth flux is resumed). This has been attributed to diffusion of atoms out of the grain boundary. In electrodeposited Cu, there was significant irreversible change as well as reversible change in the stress-thickness during the pauses. The irreversible change was attributed to grain growth in the deposited Cu layers.

The lack of significant grain growth during the pauses was further confirmed by comparing the stress evolution and grain size evolution during continuous growth with interrupted growth, as shown in Figure 3. The blue triangles represent continuous growth, and the green circles represent growth with periodic pauses of approximately two minutes. The grain size evolution and stress evolution for continuous growth and paused growth are similar, which indicates that there is no significant grain growth during the pause. This phenomenon in electrodeposited Ni films is quite different from stress-thickness evolution in evaporated Ni films, where a large amount of grain growth was observed.

The data in Figure 3b shows that there is some grain growth as the film grows, increasing from the range of 300–400 nm at 1000 nm thickness to 600–700 nm at 5000 nm. However, the rate of grain growth is slow so that it is not affected significantly by the pauses. It also does not significantly affect the determination of the steady-state stress from the slope of the stress-thickness. However, the changing grain size does make it possible to measure the stress at different grain sizes as discussed below.

Measurements of stress-thickness vs. thickness for multiple intervals of growth at different rates are shown in Figure 4c. The growth rate for each interval is shown above the stress-thickness data in Figure 4b. The growth was continued until the stress-thickness reached a constant slope that was used to determine the steady-state stress. The growth was paused between each interval at the thicknesses indicated by the dashed vertical lines. The continuity of the stress between
Dependence of steady-state stress on growth rate, grain size, and solution.—From measurements at different growth rates and film thickness, the dependence of the steady-state stress on the growth rate and the grain size could be determined, as shown in Figure 5. Because the grain size could not be held constant, the measurements were pooled into different grain size regimes within 100 nm of the nominal value: 300 ± 100, 500 ± 100 and 700 ± 100 nm. These measurements were made on samples grown in the same solution concentration of 0.36 mol/L Ni sulfamate and 0.65 mol/L boric acid. The solid lines in the figure are fits to an analytical model that is discussed below. For each of the grain size regimes, the stress has a small compressive value at the lowest growth rates. The stress becomes more tensile at higher growth rates. The maximum tensile stress at the highest growth rate appears to depend on the grain size, becoming more tensile for the films with the smaller grain size. This dependence on the growth rate and grain size is similar to what has been observed in Cu electrodeposition.14,15

To explore the effect of the electrolyte concentration, similar measurements of stress vs. growth rate and grain size were performed for different concentrations of Ni sulfamate (0.18, 0.36 and 0.50 mol/L) with the same concentration of boric acid (0.65 mol/L). These measurements are shown in Figure 6 for different grain size regimes: a) 300 ± 100, b) 500 ± 100 and c) 700 ± 100 nm. Each panel shows the results for different concentrations, corresponding to the symbols as described in the figure caption. The data indicates that there is not a strong dependence on the Ni sulfamate concentration for similar growth rate and grain size at the same boric acid concentration.

Measurements of stress vs. growth rate for varied boric acid concentrations (0.18 and 0.65 mol/L) and fixed Ni sulfamate concentration of 0.36 mol/L are shown in Figure 7. These films had measured grain sizes in the range of 300 ± 100 nm. As can be seen from the figures, the boric acid concentration, at constant Ni sulfamate concentration, has a much larger effect on the steady state stress than the Ni sulfamate concentration does at constant boric acid. The stress was significantly more tensile at large growth rates for the higher boric acid concentrations.

Analysis and Discussion

The measurements described above were designed to separate out the effects of different parameters on the stress evolution: growth rate, grain size, Ni sulfamate concentration, and boric acid concentration. It is important to do them this way because these parameters may not be independent. For instance, changing the growth rate changes the stress but it can also affect the grain size. We cannot determine the individual contribution of the growth rate or grain size to the stress change unless both parameters are characterized simultaneously.

In the following discussion, we interpret the measurements of stress vs. growth rate in terms of an analytical model that we have
developed. We use this model to extract model parameters for the different solution concentrations and grain sizes. In the final section, we try to relate the dependence of these parameters on the solution concentration to the underlying electrochemical processes controlling film growth.

Kinetic model for steady-state stress during growth.—This model has been previously described,\textsuperscript{25,27} so only a brief description is given here. It focuses on the stress generated at the triple junction where a new segment of grain boundary forms when adjacent islands grow here. It focuses on the stress generated at the triple junction where new grain boundaries, even at the expense of inducing stress in the underlying layers.\textsuperscript{26} At the top of the triple junction, both tensile and compressive stress generation mechanisms are active as the film grows. The tensile stress formation mechanism was originally proposed by Hoffman.\textsuperscript{27} It predicts that free surfaces between adjacent islands will close to form grain boundaries, even at the expense of inducing stress in the film, as long as the decrease in interfacial energy (\(\Delta \gamma\)) is more than the increase in elastic strain energy. The resulting stress is predicted to depend on \((\mathbb{M}f/\Delta \gamma )^{1/2}\).

The compressive stress is based on a mechanism proposed by Chasen et al.\textsuperscript{28} Compressive stress is assumed to arise from adatoms on the surface diffusing into the grain boundary driven by the non-equilibrium conditions on the growing film surface. The stress also raises the chemical potential of atoms in the grain boundary and enhances the diffusion of atoms from the grain boundary to the surface.

These mechanisms are combined to predict the steady-state stress in the layer for different growth conditions and grain sizes:

\[
\sigma_{\text{inc}} = \sigma_t + (\sigma_s(L) - \sigma_t) \exp\left(\frac{\beta D}{RL}\right)
\]  

where \(\sigma_t\) is the compressive stress resulting from the supersaturation on the surface during deposition. \(\sigma_s(L)\) is the tensile stress due to the formation of grain boundary and depends on the grain size. \(\beta\) is a dimensionless material parameter that includes the concentration of mobile atoms on the surface. \(D\) is the effective diffusivity for transitions of atoms from the surface to the grain boundary and \(R\) is the average growth rate of the film. The exponential term expresses the balance between the processes, making the stress more tensile for lower diffusivity or higher growth rate and more compressive for higher diffusivity or lower growth rate.

Comparison of experimental results with models.—For comparison of the experimental results with the kinetic model, a non-linear least square fitting routine was used to fit the data to Equation 6. The parameters obtained from the fitting are shown in Table II for each set of concentrations of Ni sulfamate and boric acid studied. Different values of \(\sigma_t\) are shown for each concentration that correspond to each grain size group; the fitting was done for each case using the nominal grain sizes of 300, 500 or 700 nm. There is only one value of \(\sigma_c\) and \(\beta D\) since these parameters are assumed to be independent of the grain size.

| Concentration (mol/L) | 0.18 Ni | 0.36 Ni | 0.50 Ni | 0.36 Ni |
|-----------------------|---------|---------|---------|---------|
| 0.65 acid             | -31.6   | -50.1   | -72.5   | 0.0     |
| 0.65 acid             | 313     | 534     | 501     | 446     |
| 386.4                 | 502.8   | 456.7   | 155.0   |
| 256.2                 | 346.4   | 273.4   | N/A     |
| 212.8                 | 223.5   | N/A     |

\[
\sigma_{T} (\text{MPa}) = \sigma_{T} (\text{MPa}) + \beta D (\text{nm}^2/\text{s})
\]

\[
\sigma_{T} (\text{MPa}) = N/A
\]

\[
\sigma_{T} (\text{MPa}) = N/A
\]

We have not provided estimates of the error on the fitting parameters in the table. Error bars can be determined for fitting parameters when the error is due primarily to experimental error in the measurements. This is not the case in our work since the model is not exact due to simplifying assumption. The least-squares minimization should be thought of as a way to obtain the best agreement between the model and the data, without providing the statistical significance of the parameter.

The results of the fitting using these parameters are shown as the solid lines in Figures 5, 6 and 7. For all cases, the calculated stress vs. growth rate has similar behavior to the measurements. It has a small compressive value at low growth rates and becomes more tensile at higher growth rates.

The effect of grain size in the calculations can be seen in Figure 5 for one set of concentrations (0.36 mol/L Ni sulfamate and 0.65 mol/L boric acid). The calculations were done with one value for each of \(\sigma_c\) and \(\beta D\) and different values of \(\sigma_t\) for each grain size regime. The dependence of the fitting parameter \(\sigma_t\) on grain size is shown in Figure 8; it appears to depend on \(\mathbb{M}f/\Delta \gamma\) (shown as the dashed line). Although this is different than the \((\mathbb{M}f/\Delta \gamma)^{1/2}\) predicted by Hoffman, more data is needed to determine the significance of this result. Because of the decrease in \(\sigma_t\) at larger \(L\), the calculated stress is more tensile for smaller grain size at high growth rates. At low growth rates, the model predicts a cross-over behavior in which the smaller grain size is more compressive. This is attributed to atoms being inserted into more grain boundaries as the grain size decreases in the lower growth rate regime. Although it is difficult to definitively observe this cross-over in the experimental data, it has been seen before in other systems.\textsuperscript{4,14,29}

Relating the stress and electrodeposition conditions.—In this section, we discuss what the fitting results may indicate about the connection between the stress and the process of Ni electrodeposition. The measurements and fitting results in Figures 6a–6c suggest that the stress vs. growth rate does not depend significantly on the Ni sulfamate concentration for a constant boric acid concentration. Before doing this work, our initial expectations were that changing the Ni sulfamate concentration would lead to a higher concentration of mobile adatoms on the Ni surface. This would have led to an increase in the \(\beta D\) parameter and a corresponding decrease in the tensile stress for the same growth rate. Since there is no significant change, this suggests that boric acid is playing an important role in the deposition process and resultant adatom mobility.

Some insight into this may be obtained by considering the exchange current and its dependence on the Ni sulfamate and boric acid concentration. The exchange current can be thought of as the rate at which atoms leave and return to the surface when there is no driving force applied. Therefore, the mobility of surface adatoms may be expected to be higher when the exchange current is higher. The values (shown in Table III) were determined from Tafel plots

![Figure 8](image_url)

The dependence of the fitting parameter, \(\sigma_t\), on the grain size. The dashed line corresponds to a fit of the data to a \(\mathbb{M}f/\Delta \gamma\) dependence.

Table II. Fitting parameters from the kinetic model for different concentrations. The values labelled Ni and acid refer to Ni sulfamate and boric acid concentrations, respectively.

Some insight into this may be obtained by considering the exchange current and its dependence on the Ni sulfamate and boric acid concentration. The exchange current can be thought of as the rate at which atoms leave and return to the surface when there is no driving force applied. Therefore, the mobility of surface adatoms may be expected to be higher when the exchange current is higher. The values (shown in Table III) were determined from Tafel plots.
of the overpotential and current corrected for the efficiency. The results show that the exchange current depends very weakly on the Ni sulfamate concentration for a constant boric acid concentration. The results show that the exchange current depends very weakly on the Ni sulfamate concentration for a constant boric acid concentration. This is somewhat surprising since the sulfamate concentration would be expected to affect the exchange current density. Alternatively, the exchange current is higher at larger boric acid concentration for the same Ni sulfamate concentration. The observation of Ni plating rate being primarily limited in Ni plating baths by boric acid concentration is consistent with the observations of Hoare, et al. 10,30 and Tsuru, et al. 16 The observations of Tsuru are particularly relevant as a similar of what is observed. The weak dependence of the other parameters levels of oxygen being incorporated into the film which could increase consistent with literature observations of lower oxygen incorporation and lead to stronger interfacial bonding at the grain boundary. This is $$\frac{\sigma}{\Delta \gamma}$$, the parameter for the two boric acid concentrations, up to 0.81 mol L$$^{-1}$$. With increased boric acid concentrations providing more stability to the P and higher plating efficiencies. For this study the key finding is that the stress during plating was more strongly linked to the plating rate which is highly dependent on boric acid concentration.

Alternatively, the stress does appear to depend on the boric acid concentration in Figure 7. In terms of the kinetic model, the large difference in tensile stress at high growth rate in the fitting is mostly due to the large difference in the $$\sigma$$ parameter for the two boric acid concentrations (0.18 and 0.65 mol/L). Although we acknowledge that there is limited data, it is interesting to speculate about why this might be occurring. Since the data was collected for approximately the same grain size, the change in $$\sigma$$ may be due to changes in the modulus $$M$$ or the interfacial energy $$\Delta \gamma$$. For the case of interfacial energy $$\Delta \gamma$$, the higher boric acid concentration may inhibit oxide formation and lead to stronger interfacial bonding at the grain boundary. This is consistent with literature observations of lower oxygen incorporation at higher deposition rates. 6 It has been suggested that the interfacial strength can be measured by mechanical testing of films grown under different conditions 13 but this has not been done here. Previous literature works found the modulus of Ni electroplated from Ni sulfamate baths generally decrease with increasing plating rates. 32,33 Therefore, it is not unreasonable to expect the plating conditions to affect the film modulus. Lower boric acid concentrations may contribute to higher levels of oxygen being incorporated into the film which could increase the modulus. However, this would have the effect of making the stress more tensile for lower boric acid concentrations, which is the opposite of what is observed. The weak dependence of the other parameters $$\beta$$ and $$\sigma$$ on the boric acid concentration is not sufficient to explain the change in stress.

As discussed in the introduction, there is currently no consensus as to the role of boric acid during electrodeposition of Ni from Ni sulfamate baths. 3,16 In this study, we found that the increase in boric acid concentration resulted in increased plating efficiency which is consistent with the observations of Hoare. 10 Their work indicates that the addition of boric acid to Ni plating solutions results in the onset of Ni plating becoming less negative. This decrease in plating potential causes the Ni plating potential to move from being larger than the hydrogen evolution peak to being smaller. This decreases the rate of hydrogen evolution at the Ni surface during plating, which has been confirmed by Tsuru. Tsuru demonstrated that the local pH at the Ni surface increased when the boric acid level was decreased. However, as previously stated the work of Hearne and Floro 7 found that atomic hydrogen at the plating surface resulted in a small reversible stress caused by hydrogen insertion. Our observations found that the decrease in boric acid resulted in a decreased exchange current. Though not conclusive, this could indicate that the role of the hydrogen created at the surface is to decrease the overall exchange current impacting the adatom mobility in turn increasing the observed tensile stress.

**Conclusions**

We have conducted wafer curvature measurements and cross-sectional measurements on electrodeposited Ni films to study the dependence of stress on growth rate, grain size and electrolyte concentration. The results show that the stress is more tensile at higher growth rates and this is enhanced at smaller grain sizes. Ni sulfamate and boric acid concentrations in the electrolytes affect the stress evolution in different ways. The Ni sulfamate concentration has a very weak (or no) influence on stress evolution for a fixed boric acid concentration. In contrast, higher boric acid concentration for the same Ni sulfamate concentration makes the film more tensile. The experimental results were interpreted in terms of a kinetic model which focuses on the stress generated at the triple junction where adjacent islands coalesce. A quantitative understanding of how film stress depends on growth rate, grain size and electrolyte concentrations in electrodeposited Ni is necessary in order to determine the fundamental mechanisms controlling it. Ultimately, we hope to use this knowledge to develop validated models that can predict the stress for different processing conditions. This will allow the stress to be efficiently optimized without performing a large number of deposition runs.

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**Table III. Exchange current for different bath concentrations.**

| Ni sulfamate (mol/L) | Boric acid (mol/L) | Exchange current density (mA/cm²) |
|---------------------|-------------------|----------------------------------|
| 0.18                | 0.65              | 1.671                            |
| 0.36                | 0.65              | 1.610                            |
| 0.50                | 0.65              | 1.743                            |
| 0.36                | 0.18              | 1.296                            |

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