The use of electrodeposited Co-based materials has attracted much attention over the past several decades owing in part to their interesting magnetic,1−3 and catalytic properties.4−11 These properties are largely dependent upon the structure and morphology of the electrodeposited, which in the case of cobalt can vary dramatically with overpotential, electrolyte pH, and the presence of strongly adsorbing anions.12−16 For example, solutions with a pH < 2.5 will generally result in a mixture of both face-centered cubic (fcc) and hexagonal close-packed (hcp) Co on Au.12,14,17 While more alkaline solutions yield nearly pure hcp Co.12,17−19 The magnetic properties of Co are particularly structure sensitive. Ultrathin (< 2 nm) Co, electrodeposited onto Au (111), exhibits perpendicular magnetic anisotropy and highly square hysteresis loops, identical to that of vacuum deposited Co/Au films.1,20 For Co thickness greater than 2 nm, the easy magnetization axis re-orients into the film plane.

The structure of ultrathin Co on Au (111) has been extensively studied.12,13,17−19 Non-complexing electrolytes based on sulfate or perchlorate supporting electrolyte (pH 4) form a hexagonal close-packed layer structure with the c-axis perpendicular to the Au (111) plane. A biatomic Co layer rapidly covers the Au surface, resulting in a hexagonal Moiré pattern that indicates the Co grows epitaxially, but not pseudomorphically on the Au (111).21,12,13,18,19 The Au-Au atomic distances were 0.29 nm whereas the Co-Co atomic distances were 0.261 nm, which is consistent with a hcp Co (0001) surface that is strained by about 4%. The Moiré pattern is also present after a third layer of Co is deposited; however, the strain in the Co is reduced to about 2.5%. Further growth proceeds in a layer-by-layer fashion, which leads to flat deposits on the atomic scale.

There is some debate in the literature as to whether or not underpotential deposition ( upd ) of Co occurs on Au. Several factors suggest that Co upd should in fact not take place. The equilibrium phase diagram indicates that Co and Au do not form bulk alloys at room temperature suggesting that the Au-Co interaction is weak. In addition, the surface energy of Co is greater than that of Au,22 although the adsorption of hydrogen could alter the energetics.23 Experimental studies in sulfate and perchlorate supporting electrolyte, even in the presence of chloride, show no evidence for Co upd on Au (111).12,14,18,23 However, Co upd has been reported from 5 × 10−4 mol/L H2SO417 and from slightly acidified K2SO4 electrolyte containing KSCN.14 In the latter case, the 14% strain in the Co layer required to maintain registry with the underlying Au is at least partially stabilized by adsorbed SCN− on the Co monolayer.14 Co upd has also been reported from NH4Cl electrolyte (pH 9.5) where the Co2+ in solution is present as the [Co(NH3)6(H2O)]2+ complex.15,24

In situ wafer/cantilever curvature techniques nicely complement traditional electrochemical measurements during electrodeposition. For example, cantilever curvature has been used to quantify the surface stress induced by surface charge (electrocapillarity)25−28 and adsorption processes29−32 as well as the growth stress associated with upd33−44 and the electrodeposition of bulk thin films.45−53 This method is particularly useful in identifying structural changes, such as surface alloying, that may proceed without any electrochemical or nanogravimetric signature.54,55 In the case of Co deposition, Cammarata reported that Co, galvanostatically electrodeposited onto amorphous NiTi, shows compressive-tensile-compressive (CTC) stress transitions that are typically observed for Volmer-Weber growth.56 CTC behavior is attributed to the nucleation of 3-D islands, their coalescence, and finally their thickening as a continuous film.57 However to the best of our knowledge, no in depth analysis of stress generation during the electrodeposition of Co onto (111)-textured Au substrates has been reported.

To this end, we herein report the surface and growth stress associated with electrodeposition of Co films onto (111)-textured Au cantilever electrodes from 0.1 mol/L NaClO4 containing 0.001 mol/L Co(ClO4)2. Stress measurements on these Co films, up to 100 monolayers (ML) thick, allow us to examine the surface stress change associated with the initial stages of deposition of Co onto the Au (111) surface, as well as the residual stress associated with continued growth of the Co film. We have measured the average biaxial film stress as a function of overpotential and observe a significant increase in tensile stress as the deposition potential is made more negative. These results are discussed in the context of stress generating models that appear in the literature.

Experimental

In situ stress measurements were made on a vibration-isolating optical bench using the cantilever bending method. The cantilever was a borosilicate glass (Schott North America, Inc.) strip measuring
60 mm × 3 mm × 0.108 mm. The Young’s modulus and Poisson ratio of the glass cantilever were 72.9 × 10^9 N/m^2 and 0.208, respectively. A 5 mm thick adhesion layer of titanium (Ti) and a subsequent 250 nm film of gold (Au) were vapor-deposited onto one side of the cantilever by electron-beam evaporation. The Au electrode had a (111) crystallographic orientation. The (200) reflection was not apparent in 0–20 X-ray scans and rocking curves of the (111) reflection generally yielded a full width half-maximum on the order of 2°. The curvature of the substrate was monitored while in the electrolyte and under potential control by reflecting a HeNe laser off of the glass/metal interface onto a position-sensitive detector (PSD). The relationship between the force per cantilever beam width, ΔF, exerted by processes occurring on the electrode surface and the change in radius of curvature of the cantilever, ΔR, is given by Stoney’s equation:

\[
\Delta F = \frac{Eh^2}{6(1 - \nu)} \Delta R
\]

where E, ν, and h are the Young’s modulus, Poisson ratio, and thickness of the glass substrate respectively. In the earliest stages of metal deposition, several factors including surface stress, interfacial stress, and misfit stress, contribute to the measured ΔF. However, as the deposited film thickens, and contributions from the surface and interface become less important, ΔF is equal to the stress-thickness product, σh, i.e., the average biaxial film stress, σ, multiplied by the thickness of the film, h. Since the stress in polycrystalline films is generally not uniform through its thickness, the average stress is obtained from the integral of the stress over the thickness of the film,

\[
\sigma = \frac{1}{h} \int_0^h \sigma(z) dz
\]

where σ(z) is the in-plane stress in the film at a distance z from the substrate. A single stationary laser measures only the change in curvature, rather than absolute curvature, by measuring the deflection of the cantilever. A small angle approximation was used to estimate the curvature of the glass cantilever directly from the reflected laser position on the PSD. ΔF is arbitrarily referenced to zero at the beginning of the experiment or measurement. A more detailed description of the optical bench and stress measurement is published elsewhere.35,52

The electrolyte was 0.1 mol/L NaClO4 (Aldrich, 99.999%) + 0.001 mol/L Co(ClO4)2 (Alfa Aesar, Reagent Grade) and was prepared using 18.3 MΩ-cm ultrapure water (Barnstead). The pH of the solution was 4.8. The electrochemical cell was a single-compartment borosilicate cell covered by a polytetrafluoroethylene cap. A glass disk was joined to the back of the cell to allow it to be held and positioned by a standard mirror mount on the optical bench. The electrode holder that clamped the top of the cantilever electrode was submerged in the electrolyte so the entire length of cantilever was electrochemically active. A typical immersion length was 22 mm, leading to an exposed area of 0.66 cm^2. The counter electrode was a platinum foil placed parallel to and in the same solution as the working electrode. The reference electrode was a saturated mercury-mercurous sulfate electrode referenced to the SSE. Potential control was maintained using an EG&G Princeton Applied Research Corp. (PARC) model 273 potentiostat-galvanostat. Prior to introduction into the cell, the solution was thoroughly de-aerated by bubbling high purity Ar. Ar flow was maintained in the headspace of the cell during measurements. The EQNB measurements both the resonant frequency and the resistance R0 of the equivalent resonant circuit. R0 in all measurements changed very little, confirming that no significant roughening of the electrode surface took place.

X-Ray Diffraction was performed using a Siemens D-500 diffractometer with Cu-Kα radiation in 0–20 mode. Fixed θ–2θ measurements were made using a Bruker D8 diffractometer with Vantec 500 area detector and Cu-Kα radiation. SEM images were obtained using a JEOL JSM-7400 FE-SEM with an accelerating voltage of 10–15 kV and a working distance of 6–10 mm.

Results

Potentiodynamic behavior and stress measurements.—Figure 1 shows the cyclic voltammetry (CV) and associated stress response for Co deposition onto Au. The CV shows a small peak at −1.0 V, due to the reduction of H⁺ on the Au surface. In more acidic solution, higher H⁺ concentrations would lead to significant hydrogen evolution reaction (HER), however, due to the relatively high pH, the generation of H₂ from H⁺ is under diffusion rather than kinetic limitations. This peak is followed by the reduction of Co²⁺ at −1.2 V, with increasing overpotential eventually leading to H₂O reduction. The equilibrium potential for Co²⁺ reduction in 0.001 mol/L solution is −1.032 V SSE. According to the Fig.1 voltammetry, a 0.2 V cathodic overpotential is required to trigger Co²⁺ reduction on Au in this electrolyte. The anodic crossover on the return sweep occurs at a potential of −1.08 V, which is considerably closer to the equilibrium potential. A high overpotential for the reduction of Co has been documented by many groups:4,12,14,17–19,23,24,59 Upon anodic scanning, the Co is dissolved at a potential of −0.8 V, showing slightly irreversible reduction/oxidation of Co. It should also be noted that we observe no evidence for Co UPD on Au, as UPD peaks should appear at ~−0.6 V.14 UPD of Co on Au has been shown to depend on both pH53 and the presence of adsorbing anions such as SCN⁻.14

The accompanying stress signature shows that prior to Co reduction, there is a slight increase in the tensile direction owing to electrocapillarity as well as the desorption of ClO₄⁻ from the Au surface.60,61 The latter contribution is particularly relevant as the potential approaches the potential of zero charge (PZC), which is −0.2 V for Au at this pH and electrolyte.61,62 Upon the initial reduction of Co²⁺, the stress initially becomes compressive (by about −0.2 N/m)
before turning back to the tensile direction. The negative electric charge associated with the peak in the compressive stress is about 500 μC/cm². Considering a 2-electron reduction process, this corresponds to less than 1 monolayer of cobalt metal, assuming that 590 μC/cm² is required to deposit an incommensurate close-packed monolayer. Following this initial compressive stress, only tensile stress is generated. Little stress change is observed at potentials more negative than −1.4 V, reflecting the very low faradaic efficiency for Co deposition once the potential for H₂O reduction is reached. On the reverse sweep, additional tensile stress is produced until dissolution of Co occurs further along the anodic cycle.

**Steady-state tensile deposition: Faradaic efficiency.**—In order to examine the growth stress that develops in electrodeposited Co thin films, the faradaic efficiency of the deposition process was determined in conjunction with the stress measurement by using stripping voltammetry, a technique commonly used in the Co deposition literature.12,13,63 As shown in Figure 2a, the electrode potential was stepped from a starting potential of −0.6 V to the deposition potential of interest and poised for sufficient time to deposit approximately 20 nm of Co. Following deposition, the electrode was allowed to equilibrate at the open circuit potential (about −1.0 V) for 20 s prior to initiating an anodic voltammetric sweep at 2 mV/s until the deposit was completely removed. The curvature of the cantilever was monitored throughout the measurement. The example shown in Fig. 2a shows a deposition charge of −91.3 mC/cm² and a stripping charge of +60.8 mC/cm², resulting in a faradaic efficiency of 60.8% for Co deposition. The deposition charge density was then scaled by the faradaic efficiency in order to determine the deposit thickness for the stress measurement.

In order to verify that stripping voltammetry provides an accurate measure of the faradaic current efficiency for Co deposition, a series of measurements were made using the EQNB. Figure 2b shows various mass-charge ratios as a function of Co deposition potential. The quantity qₐ/qₜ (red) is the coulombic efficiency; i.e., the ratio of the anodic stripping charge to the cathodic deposition charge. This quantity is accessible during the stress measurement. It has values ranging from about 90% near the Co equilibrium potential to about 70% at more negative deposition potential. The quantity mₐ/qₜ (blue) is the ratio of the deposition mass to the deposition charge, normalized to the theoretical value of 0.305 mg/C for Co deposition from Co²⁺. The potential dependence of mₐ/qₜ and qₐ/qₜ are very similar. The final quantity, mₐ/mₐ (black) is the ratio of the anodic stripping mass to the cathodic deposition mass. This quantifies the mass gained during deposition that is electrochemically active during anodic stripping. Taken together, the data suggests that Co deposition is 70 – 90% efficient, with the remaining current producing hydrogen. This is effectively quantified by qₐ/qₜ, which can easily be obtained from stripping voltammetry. The data also suggests that at the more negative deposition potentials, Co(OH)₂ is precipitated during Co deposition due to a pH increase near the electrode surface as a result of H₂ evolution.

**Steady-state deposition.**—Cobalt films with targeted thicknesses of about 20 nm were electrodeposited at potentials ranging from −1.18 V to −1.28 V. This potential range is positive of the H₂O reduction potential, based on the results from Figure 1. Figure 3 shows the current transients for deposition at various overpotentials. The inset highlights the first 25 s of deposition. At nearly all overpotentials, the current shows a peak following double layer charging but prior to transitioning to the steady-state current, suggesting the formation of discrete nuclei in the early stages of deposition. The current decrease

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**Figure 2.** (a) Chronoamperometry response for Co electrodeposition onto Au cantilever electrodes in 0.1 mol/L NaClO₄ containing 1.0 × 10⁻³ mol/L Co(ClO₄)₂. The potential was stepped from −0.6 V to the deposition potential of interest for 1200 s. Following deposition the electrode was allowed to equilibrate at the open circuit potential (about −1.0 V) for 20 s prior to initiating an anodic voltammetric sweep at 2 mV/s until the deposit was completely removed. (b) EQNB mass-charge ratios as a function of Co deposition potential, obtained from stripping voltammetry measurements similar to (a); qₐ/qₜ (red) is the ratio of the anodic stripping charge to the cathodic deposition charge, mₐ/qₜ (blue) is the ratio of the deposition mass to the deposition charge normalized to the theoretical value (305 mg/C) for Co deposition, and mₐ/mₐ (black) is the ratio of the anodic stripping mass to the cathodic deposition mass.

**Figure 3.** Chronoamperometry response for Co electrodeposition onto Au cantilever electrodes in 0.1 mol/L NaClO₄ containing 1.0 × 10⁻³ mol/L Co(ClO₄)₂ for several deposition potentials. The inset highlights the first 25 s of deposition.
follows \( t^{-1/2} \) time dependence, reflecting the expanding diffusion layer thickness. The steady state current ranges from 67 \( \mu \text{A/cm}^2 \) at \(-1.18 \text{ V} \) to the diffusion limited value of 79 \( \mu \text{A/cm}^2 \), which was achieved at \(-1.26 \text{ V} \). However as pointed out earlier, the current efficiency for the cobalt reduction ranges from ca. 90% down to ca. 70% over this range of potentials so the deposition rate actually decreases slightly with increased overpotential.

The stress response associated with the Figure 3 chronoaamperometry is shown in Figure 4. The deposit thickness was calculated from the integrated current density, after multiplying by the corresponding steady state current efficiency obtained from the stripping voltammetry. All of the stress-thickness curves reach steady state after a thickness of about 5 to 8 nm. The initial compressive stress that was observed in the Figure 1 voltammetry is readily apparent in the Figure 4 inset, which highlights the first 1 nm of deposition. In nearly all cases, the compressive stress is limited to the first monolayer, after which only tensile stress is generated. The possible origins of this compressive stress will be discussed later. It is also interesting to note in the Figure 4 inset the sequential nature of the stress response to the potential step. For example, when the potential is stepped from \(-0.6 \text{ V} \) down to the desired deposition potential, the initial \(+0.15 \text{ N/m} \) tensile stress is the response associated with electrocapillarity and anion desorption, similar to that observed in the Figure 1 voltammetry. Even following a potential pulse, the stress transient captures all stages of the charging and deposition process. Although not shown in Figure 4, all of the stress-thickness values return to within 0.1 N/m of the initial 0 value following Co dissolution from the Au surface, indicating that the stress is due exclusively to the Co electrodepos and that the Au surface is not significantly altered by Co deposition and stripping.

Returning to the stress-thickness curves in Figure 4, assuming that the stress in previously deposited Co 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 Co being deposited at the surface where \( z = h \). We will refer to the linear region where the incremental stress is constant as the steady-state stress, \( \sigma_{ss} \), where

\[
\sigma_{ss} = \frac{d(h_{f})}{dh} \tag{3}
\]

for values of \( h \) where the slope \( d(h_{f})/dh \) is constant. If we evaluate the slope in the linear region, the steady state stress values range from 0 MPa to about 450 MPa, increasing at more negative deposition potentials, as shown in Figure 5. An increase in tensile stress with overpotential (i.e., growth rate) is a common feature of the Fe-group metals\(^{50,66} \) and their alloys\(^{64–69} \). This is often attributed to a decrease in grain size, which increases the coalescence-induced tensile stress.\(^{60,66,68} \) However it should be noted that stress models appear in the literature that predict increasingly tensile growth stress with increased growth rate, even for fixed grain size.\(^{70} \)

**Deposit structure.**—Figure 6a shows representative X-ray diffraction patterns for the (111)-textured Au substrate (A) and two Co electrodeposits (B,C). Patterns (A) and (B) were run in conventional 0-20 mode; i.e., the reciprocal lattice vector is perpendicular to the plane of the film. Pattern (A) shows that the evaporated Au film has a strong (111) crystallographic texture as only the 111 and 222 reflections are observed. Pattern (B) shows the diffraction pattern for a 80 nm Co electrodeposit. The Co has adopted the texture of the Au substrate in that only two reflections are observed. This is consistent with several reports in the literature indicating that the Co grows epitaxially, but not pseudomorphically on Au (111).\(^{12,14,18} \) However the Co reflections shown in Figure 6a, pattern (B), can be indexed to fcc 111 and 222 as well as hcp 002 and 004. According to the JCPDS (85-0727 and #15-806), the d-spacing for the hcp 002 is smaller than the fcc 111 by about 1.2%. This would suggest that a structural determination could be made based on peak location alone. However, the fairly large biaxial tensile stresses in these films gives rise to an out of plane lattice contraction ranging from about 0.1 to 0.3% which makes a structural determination based on X-ray diffraction difficult.

Although the reflections expected for randomly oriented polycrystalline material do not appear for highly textured films when examined in 0-20 mode, they can be specifically targeted using the appropriate 20-20 scan. The diagram in Figure 6b shows the Bragg conditions for interrogating the (220) and (311) for fcc Co as well as the (103) for hcp Co. The solid lines in the figure show the plane normals with respect to the (111) normal. We define this angle as \( \phi \). The incident X-ray beam is set at a fixed angle of \( \omega \). This value is determined from the Bragg angle, \( \theta \), minus the angular offset from the (111), \( \phi \). For example, in order to probe the film for fcc (220) planes, \( \omega \) is set at 2.67° which is obtained from \( \theta_{220} - \phi_{220} = 37.93° - 35.26° \). The detector is then scanned to capture the 20 for the reflection of interest, and a diffraction peak is observed when the X-ray scattering vector and the (220) reciprocal lattice vector coincide. Pattern (C) in Figure 6a
Figure 6. (a) X-ray diffraction patterns of (A) Au substrate in $\theta$-2$\theta$ mode; (B) 80 nm film of Co electrodeposited onto Au substrate at a potential of $-1.25$ V, in $\theta$-2$\theta$ mode; (C) 35 nm film of Co electrodeposited onto Au substrate at a potential of $-1.4$ V, combined patterns of three separate $\omega$-2$\theta$ scans under conditions shown in (b). (b) Diagram showing settings for the $\omega$-2$\theta$ scans shown in a(C). The solid lines represent the plane normals for fcc (220), fcc (311), and hcp (103) for the (111)-textured Co film. The dashed lines show the Bragg conditions for these planes, where $\omega$ is the angle between the Co film and the incident X-ray beam.

is a composite of the three measurements made for the fcc (220) and (311) and hcp (103) for a 35 nm Co film deposited at $-1.4$ V. Both fcc reflections are reasonably strong whereas the reflection for hcp (103) is not readily apparent, indicating that the Co films examined here have primarily a fcc structure.

Deposit morphology.—Figure 7a shows a scanning electron micrograph (secondary electron image) of the evaporated Au substrate. The average grain size is about 100 nm. As mentioned previously, the Au has a (111) fiber texture; i.e., the grains are oriented (111) out-of plane and have a random orientation in-plane. Figure 7b is a similar image of a 80 nm thick Co film electrodeposited at a potential of $-1.25$ V. The surface consists of relatively flat grains that appear to exceed the grain size of the Au substrate. Based on visual inspection of the micrograph, we estimate the Co grains to be 200 $\pm$ 35 nm in diameter. The micrograph also suggests that the Co film grows by two-dimensional island growth, resulting in a relatively flat deposit, at least for thicknesses approaching 100 nm. Electron backscatter diffraction (EBSD) patterns of the as-deposited surface (not shown) indicate that most of the Co grains have the fcc structure; however approximately 10% of the grains examined clearly show hcp symmetry. This is consistent with the X-ray analysis. Although the Co films are primary fcc, regions of hcp do exist.

Discussion
The evolution of residual stress during thin film growth depends on several factors including deposit microstructure, growth conditions, and properties of the material being deposited. In the absence of misfit stress, tensile stress generally dominates the early stages of film growth as discrete nuclei coalesce into a continuous film.57 However, as films become thicker and the height becomes more uniform, the stress often reaches a constant steady-state value. Models have been developed that treat this 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.70 Growth of low mobility materials at low temperature or at high growth rates tends to produce films with large tensile stresses. Alternatively, growth of high mobility materials at high temperature or low growth rates tends to produce films with more compressive stress. The influence of growth rate on steady state stress has been nicely demonstrated in Ni, electrodeposited from surfactant-free sulfamate electrolyte.50 The stress was shown to vary from $-500$ MPa to $+500$ MPa as the growth rate, indicated by the current density, was increased while the grain structure (size and texture) remained unchanged.

Although our steady state stress results for Co (Figure 5) appear to show a similar dependence on deposition overpotential, either through increased growth rate or decreased grain size, neither of these modes are operative over this range of deposition potentials. In our case, since the Co$^{2+}$ concentration in the electrolyte is so low, Co deposition quickly becomes diffusion-limited. The corresponding decrease in current efficiency with deposition overpotential, actually results in a slight decrease in growth rate over this range of potentials. In addition, inspection of the as-deposited surface by SEM shows that the grain size remains constant, at about 200 nm. We can only conclude that...
the observed increase in tensile stress with deposition overpotential is due to other stress generating mechanisms.

We first examine the compressive stress observed during the early stages of Co deposition onto Au. This compressive stress is observed both in the Fig. 1 voltammetry and the Fig. 4 constant potential deposition experiments and is clearly associated with the cantilever's transition from a Au surface to a Co surface. Identical voltammetry experiments (not shown) on Au in the absence of Co show no compressive stress until the onset of H2O reduction at −1.4 V. The compressive stress is also absent when Co is used as a substrate. Although the Co deposition reaction is shifted about 100 mV more positive than that observed for the Au electrode, the corresponding stress response shows that only tensile stress is generated over the entire deposition cycle. Cammarata also observed compressive stress at the earliest stages of Co deposition onto amorphous NiTi.53 However, the compressive stress was associated with isolated Co nuclei roughly 200 nm in diameter and 40 nm in height, rather than the single ML observed in our experiments on Au.

The surface stress difference, ΔF, associated with geometrically strained overlayer growth can be given by

\[ \Delta F = \Delta f_s + \Delta f_{pe} + \Delta f_I + \Delta \Sigma_{ad}/h_f \]  

where \( \Delta f_s \) is the change in the intrinsic surface stress associated with the change in surface chemistry, \( \Delta f_{pe} \) is an electrocapillary term that reflects the change in the potential of zero charge (pzc) of the surface, \( \Delta f_I \) is the interface stress between the overlayer and the substrate, and \( \Delta \Sigma_{ad}/h_f \) is the product of the misfit stress and the film thickness of the overlayer. The calculated surface stress for unreconstructed Au (111) using embedded atom method potentials is about 1.5 N/m.77 However, there does not appear to be a corresponding calculation for the surface stress of Co, values for Ni and Cu are 0.43 N/m and 0.86 N/m, respectively.77 A similar value for Co would result in a compressive contribution for \( \Delta f_I \) in Eqn. 4 above. The pzc of Co is close to its deposition potential, about −1.2 V\textsuperscript{c} whereas as stated previously, the pzc for Au is considerably more positive.65,75 It has been observed experimentally that negative surface charge results in tensile surface stress.26,76,77 As a consequence, the electrocapillary contribution at the Co deposition potential will be compressive as the surface transitions from Au (net tensile from excess negative charge) to Co (net neutral at its pzc). One can then expect the first two terms of Eqn. 4 to result in compressive stress.

The interface stress (\( \Delta f_I \)) between the Co and Au is not known, although expected to be quite small. Calculated values for Ni-Au and Cu-Au are reported to be −0.08 N/m and 0.01 N/m, respectively.77,79 The final term in Eqn. 4 is the misfit term. As stated previously, STM studies clearly show that Co deposits on Au (111) single crystals tend to adopt a lattice spacing closer to Co, not Au, producing a Moiré pattern that indicates the lack of registry with the substrate.4,18,31 However, these same studies show that the Co is positively strained and that the strain is progressively reduced as the film thickens. As stated previously, 1% strain in the Co film results in a stress of about 3 GPa, or a stress-thickness product (\( \Delta \Sigma_{ad}/h_f \)) of +0.62 N/m. However, in the sub-monolayer regime where the Co exists as small islands, the surface stress acting on the clusters gives rise to a size-dependent compressive strain within the cluster that can virtually eliminate the misfit strain.78 Even as the Co approaches monolayer coverage, the misfit strain can be relaxed by adsorbed hydrogen since the Co is known to be hydrogen terminated at these potentials.12 Hydrogen adsorbed on both Pt79 and Pd80,81 show large compressive changes in surface stress. We can therefore conclude that the misfit term in Eqn. 4 only becomes a factor when the thickness of the Co exceeds a monolayer and that the compressive stress observed in the sub-monolayer regime is due to the remaining terms, i.e., surface and interface stresses.

We now examine the tensile stress and its dependence on deposition potential. STM studies show that Co on Au follows Stranski-Krastanov growth. Tensile strains of 2% have been reported for the first 3 to 4 ML of Co on Au (111),12,14,18 and remnant strains of 1% have been reported in thicker Co films (100 ML) electrodeposited onto Cu (001).82 One can then expect a strong tensile stress response, due to residual misfit strain as well as the coalescence of 2D islands. However, misfit and coalescence contributions seem to be absent from the −1.18 V deposit which exhibits very small residual stress, nor can they account for the potential dependence of the tensile stress, the latter requiring a decrease in grain size, which is not supported by microscopic analysis.

Since the H\textsuperscript{+} reduction potential is about 200 mV more positive than Co\textsuperscript{2+} reduction, H\textsuperscript{+} discharge serves as a parasitic reaction during Co deposition. Our nanogravimetric measurements indicate current efficiencies ranging from 65% to 90%, the latter observed at low overpotentials. This has several ramifications. The first being the possible precipitation of Co(OH)\textsubscript{2} due to the localized pH increase at the cathode surface. The solubility product (K\textsubscript{sp}) of Co(OH)\textsubscript{2} is reported to be 1.09×10\textsuperscript{−16}.83 In order to precipitate Co(OH)\textsubscript{2} from a 1 mmol/L solution of Co\textsuperscript{2+}, the pH must reach a value of 8.0.84,85 Simulations suggest that during H\textsubscript{2} evolution on a stationary electrode, the interfacial pH can increase 4.2 pH units from a bulk pH value of 5.0.86 sufficient to cause precipitation of Co(OH)\textsubscript{2}. In reality, a pH higher than 8.0 is required since the surface concentration of Co\textsuperscript{2+} is also decreased at the surface. In any event our EQNB data does indeed suggest that some Co(OH)\textsubscript{2} precipitation does occur on the Co surface at the more negative potentials. However, a close comparison of Figs. 2b and 5 indicates that significant tensile stress develops at intermediate potentials where little Co(OH)\textsubscript{2} precipitation is observed, suggesting that hydroxide precipitation does not play a primary role in the stress state of the Co film.

Given the fact that the tensile stress seems to track the decrease in the faradaic efficiency for Co deposition, the obvious next step is to examine the role of hydrogen. Similar to many of the Fe-group metals, the cobalt – hydrogen phase diagram exhibits some very interesting behavior.87,88 Hydrogen tends to stabilize the fcc structure, dramatically enhancing the hydrogen solubility. When exposed to hydrogen at elevated temperature, the insertion of hydrogen into the fcc Co lattice causes a lattice contraction, which is attributed to the formation of hydrogen-vacancy (H-Vac) clusters. This is supported by first-principles calculations which find that vacancy formation energies in fcc hydrides are substantially reduced by hydrogen insertion into the lattice.89 Contractions as high as 3% have been reported for Co at 950 °C and 6.8 GPa hydrogen pressure.88 Such strains would generate stresses in the GPa range if the Co were constrained and not able to contract.

Thermal desorption measurements (TDS) conducted after high temperature exposure of Fe-group metals to hydrogen can easily distinguish between H atoms desorbed from regular interstitial sites and those trapped by single vacancies and vacancy pairs.86 Interestingly, electrodeposited films of Cr, Ni, Cu, Mn, and Co exhibit thermal desorption spectra very similar to those obtained following high temperature exposure to hydrogen, indicating that electrodeposited films also consist of H-Vac defects.87,80,81 TDS analysis of electrodeposits several years old indicate that once H-Vac defects are formed, they remain stable indefinitely under ambient conditions, even after complete loss of H from regular interstitial sites. It is the loss of this interstitial H that is responsible for the additional tensile stress that develops following deposition of Fe-group metals and their alloys, even though the film is already under significant tensile stress. Such behavior has been nicely demonstrated in electrodeposited Co-Fe.69

Whereas H-Vac formation by the high-temperature exposure to hydrogen is controlled by solid-state diffusion of vacancies from the surface into the bulk, these extreme conditions can be avoided by electrodeposition where H and metal atoms are deposited simultaneously and allow for easy incorporation of vacancies. We can also expect the H-Vac defect concentration to increase as the Co faradaic efficiency decreases at the more negative deposition potentials. If we assume that the fractional lattice contraction of a H-Vac defect is similar to that of an uncomplexed vacancy (\( f_c = −0.36 \) for an fcc lattice),81,83 we can estimate that a 1% mole fraction of H-Vac defects is necessary in order to generate the 400 MPa tensile stress measured in our electrodeposited Co films.
In summary, we propose that in addition to the stress generating mechanisms commonly encountered during thin film growth; i.e., nucleation coalescence, ad-atom diffusion into grain boundaries, etc., the formation of H-Vac defects, facilitated by the cogeneration of hydrogen, can serve as a source of tensile stress in electrodeposited Fe-group metals and alloys. Although tensile stress can also be introduced post-deposition by the desorption of interstitial hydrogen, it is the stable H-Vac defects that can give rise to steady state tensile stress during deposition. In the case presented here, the decrease in the Co current efficiency is responsible for its potential dependence, under deposition conditions where both the grain size and growth rate remain constant. The formation of H-Vac defects is also consistent with the fcc structure observed in our Co electrodeposits. An inter-

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Conclusions

Co thin films were electrodeposited onto (111)-textured Au from 0.1 mol/L NaClO4 + 0.001 mol/L Co(ClO4)2 4.8) electrolyte while the growth stress was measured in situ using the cantilever bending method. XRD analysis indicated that the Co was face-centered cubic and maintained the (111) texture of the Au substrate, suggesting epitaxial but not pseudomorphic growth on the Au. Steady state tensile stress, ranging from 0 to +450 MPa, developed in continuous Co films and showed a strong dependence on electrode potential, although there was no corresponding change in grain size or growth rate, factors typically associated with stress generation. We attribute the tensile stress and its potential dependence to the formation of hydrogen stabilized vacancies, defects found to be quite stable in fcc Fe-group metals and alloys when deposited in the presence of hydrogen.

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