Electron scattering at Co(0001) surfaces: Effects of Ti and TiN capping layers

Erik Milosevic and Daniel Gall

AFFILIATIONS
Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th St., Troy, New York 12180, USA

ABSTRACT

In situ transport measurements on epitaxial 7.6-nm-thick Co(0001)/Al₂O₃(0001) films with and without Ti and TiN capping layers during O₂ exposure are used to investigate the effects of surface chemistry on electron scattering at Co(0001) surfaces. The Co sheet resistance \( R_s \) increases with increasing thickness \( d_{Ti} \) and \( d_{TiN} \) of the Ti and TiN capping layers, saturating at 8% and 31% above the uncoated Co(0001) for \( d_{Ti} > 0.2 \text{ nm} \) and \( d_{TiN} > 0.1 \text{ nm} \), respectively. This increase is attributed to electron scattering into local surface states, which is less pronounced for Ti than TiN. In situ resistance measurements taken during a continuously increasing O₂ partial pressure from 0 Pa to 40 Pa indicate a relatively steep 24% increase in \( R_s \) at an exposure of ~50 Pa s, which can be attributed to Co surface oxidation that leads to atomic level roughness and a decrease in the electron scattering specularity \( p \). Ti and TiN cap layers with \( d_{Ti} \geq 0.5 \text{ nm} \) and \( d_{TiN} \geq 0.13 \text{ nm} \) exhibit no resistance change upon air exposure, indicating suppression of Co oxidation. These results indicate a promising Co–Ti interface with an electron scattering specularity of \( p = 0.4–0.5 \), which is retained during oxygen exposure, while, in contrast, electron scattering at the Co–TiN interface is completely diffuse (\( p = 0 \)), suggesting that Ti barrier layers facilitate higher-conductivity Co interconnects than TiN barriers, as long as the Ti layer is sufficiently thick (\( d_{Ti} \geq 0.5 \text{ nm} \)) to suppress Co oxidation.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5145327

I. INTRODUCTION

Electron transport in metallic conductors at the nanometer scale is an area of considerable interest to the semiconductor industry because the resistivity of narrow interconnect wires increases signal delay and power consumption in integrated circuits. At wire dimensions near or below the bulk electron mean free path, electron scattering at surfaces, grain boundaries, and surface roughness cause the resistivity to increase well above the bulk value. The resistivity size effect in Co is of particular interest because Co is currently used in the first few metallization levels for the narrowest interconnect lines by multiple integrated circuit manufacturing companies, replacing the previous Cu and W metallization schemes due to a number of advantages, including (1) a lower melting point in comparison to W, allowing defect healing and grain growth at feasible annealing temperatures, (2) a larger electromigration resistance in comparison to Cu, and (3) thinner and more conductive barrier/adhesion layers, allowing greater volumes of metal fill and lower vertical via resistances. Electron scattering at surfaces is typically quantified using the classical model by Fuchs and Sondheimer (FS), who described electron–surface interactions phenomenologically using a specularity parameter \( p \) that adopts a value between 0 and 1. Zero specularity (\( p = 0 \)) corresponds to completely diffusive scattering, where the electron momentum is randomized upon scattering at the surface, resulting in a resistivity increase. Conversely, specular scattering (\( p = 1 \)) corresponds to electron reflection from the surface with conservation of the parallel momentum component and, therefore, no effect on the resistivity. Thus, metal surfaces/interfaces that exhibit a large electron scattering specularity are desired for next generation interconnect technologies. Surfaces with partially specular electron scattering have been reported for Ag, Au, and Cu, where the surface of Cu is observed to transition from partially specular with \( p_s = 0.6–0.7 \) in vacuum to completely diffuse upon oxidation. In addition, studies have revealed that partial specularity exists at the interfaces between Cu and SiO₂, NiO, TiO₂, AlOₓ, and TaO₅, indicating that the Cu specularity can be intentionally “tuned” with the proper choice of the capping layer.
have recently reported the growth of epitaxial Co(0001) layers and shown that oxygen exposure causes a resistance increase, which is attributed to a transition from partially specular ($p_{\parallel} = 0.55$) to diffuse ($p_{\parallel} = 0$) surface scattering upon oxygen exposure,\textsuperscript{33,34} similar to the reported effects on Cu(001) surfaces.\textsuperscript{27–29} These results suggest that the scattering peculiarity of the Co surface may also be intentionally modulated with appropriate capping layers, which motivates the study presented here.

In this article, we report on the electron scattering at the Co(0001) surface including the effects of surface oxidation, Ti capping layers, and TiN capping layers on the resistivity. In situ transport measurements from nominally 7.6-nm-thick epitaxial Co(0001) layers on c-plane sapphire during O$_2$ exposure indicate a 24% resistance increase due to a surface oxidation that results in a decrease in the electron surface scattering specularly. Ti capping layers suppress the Co oxidation effects and facilitate partially specular electron scattering at the Ti–Co interface. TiN caps also protect Co oxidation but result in a 55% resistance increase in comparison to bare Co due to a transition to diffuse scattering at the Co–TiN interface, indicating that Ti liners provide a conductivity benefit over TiN liners for Co metallization.

II. PROCEDURE

Co(0001) layers, and Ti and TiN capping layers were deposited in a three-chamber ultra-high vacuum DC magnetron sputtering system with a base pressure of 10$^{-7}$ Pa.\textsuperscript{35–37} Polished 10 × 10 × 0.5 mm$^3$ Al$_2$O$_3$(0001) substrates were cleaned ultrasonically in consecutive baths of trichloroethylene, acetone, isopropyl alcohol, and deionized water, mounted to a Mo stub with colloidal silver paint, and inserted into the deposition system through a load lock. Substrates were degassed in situ at the Co deposition temperature of 300 °C for one hour. 5-cm-diameter Co (99.95%) and Ti (99.95%) targets were positioned facing the substrate at a 45° tilt and a distance of 9 cm. They were sputter-cleaned with closed shutters for 5 min prior to Co depositions, which were done in 0.40 ± 0.03 Pa Ar (99.999%) with a continuously rotating substrate. A constant magnetron power of 50 W yielded a deposition rate of 0.10 ± 0.01 nm/s, as determined from thickness measurements by x-ray reflectivity (XRR), resulting in a nominal thickness of 7.6 nm for the Co layers deposited for 75 s. The films were left at 300 °C for 1 hour after deposition and then allowed to cool to room temperature (295 K) for approximately 12 h. Subsequently, they were transferred in situ to an attached analysis chamber for in situ resistance measurements using a linear four-point probe operated at 1–100 mA. The samples were then transferred back to the deposition chamber without air exposure for deposition of either Ti or TiN capping layers at room temperature (295 K) using a port shutter over the Ti target to limit the deposition rate. Ti caps were deposited at a magnetron power of 100 W in 0.40 Pa Ar yielding a deposition rate of 0.11 nm/min, as determined by XRR analyses. TiN caps were deposited at 100 W in 0.67 Pa N$_2$ with a deposition rate of 0.03 nm/min. The Ti deposition time was varied from 0 s to 1040 s to obtain a set of samples with varying effective Ti capping layer thicknesses $d_{Ti} = 0.2$–2.0 nm. TiN deposition times were varied from 21 s to 5536 s, yielding nominal cap thicknesses $d_{TiN} = 0.0075$–2.0 nm. The capped Co layers were then moved to the analysis chamber for additional in situ transport measurements, including measurements during oxygen exposure. For this purpose, the resistance was continuously measured while introducing a constant flux of a 90% Ar–10% O$_2$ gas mixture with the valves to the vacuum pumps closed. This leads to a linearly increasing (0.07 Pa/s) chamber pressure, reaching a 400 Pa total pressure corresponding to a ~1.6 h experiment. Finally, the samples were removed from the system via a load lock, and their ex situ sheet resistance was measured after air exposure using a second four-point probe, as recently reported for epitaxial Nb$^{+}$ and Ni$^{+}$ layers.

X-ray diffraction (XRD) analyses were performed using a PANanalytical X’pert PRO MPD system with a Cu source.  $\omega$–$2\theta$ survey scans were taken with a divergent beam and a PW3018/00 PIXcel line detector operated in scanning mode. $\varphi$ scans were acquired with a point-focus optics using a polycapillary lens that yields quasi-parallel Cu K$_\alpha$ x-rays with a <0.3° divergence, and a 0.2° parallel-plate collimator in front of a scintillation point detector. X-ray reflectivity measurements for thickness calibrations were done in the same system, using a parabolic mirror, which yields a source divergence of <0.055°, and a scintillation point detector.

III. RESULTS AND DISCUSSION

All Co layers in this study have the same nominal thickness of 7.6 nm (based on the identical deposition rate and time) and are epitaxial Co(0001) layers as confirmed by XRD methods\textsuperscript{38,39} and XRD methods and XRD methods, including $\omega$–$2\theta$ and $\varphi$ scans of the Co 0002 and 1010 reflections, indicating the epitaxial relationship: Co[0001]∥Al$_2$O$_3$(0001) and Co[1010]∥Al$_2$O$_3$(1120) as we have previously reported and described in detail in Ref. 33. The Co(0001) films have an average measured in situ resistivity of 12.0 ± 1.5 $\mu$Ω cm, where the stated error bar represents the standard deviation and indicates sample-to-sample variations, which are attributed to the differences in the effective thickness and crystalline quality. This value is similar to $\rho = 12.27 ± 0.64 \mu$Ω cm that we have previously reported for 7.9-nm-thick epitaxial Co(0001).

Figure 1 shows a plot of the change in sheet resistance $\Delta R_s$ caused by the deposition of Ti or TiN cap layers on 7.6-nm-thick Co(0001), plotted as a function of the capping layer thickness $d_{cap}$. Each data point represents the difference between the in situ measured $R_s$ of the same sample before and after deposition of the cap layer. Thus, the plotted $\Delta R_s$ is unaffected by sample-to-sample variations, and the relative uncertainty in $\Delta R_s$ is smaller than the sample-to-sample variation in $\rho$. A bare (uncoated) Co film is represented by the data points at $d_{cap} = 0$ nm, where, by definition, there is no sheet resistance change $\Delta R_s = 0 \Omega/\square$. The resistance of Co films increases when coated with Ti, indicated by an increase in $\Delta R_s$ to 0.7 ± 0.6, 1.3 ± 0.9, 1.3 ± 0.1, 0.7 ± 0.2, and 1.4 ± 0.2 $\Omega/\square$ for $d_{Ti} = 0.13$, 0.25, 0.50, 1.0, and 2.0 nm, respectively. This increase is attributed to an increasingly diffuse electron surface scattering caused by the Ti atoms that disturb the electronically smooth Co(0001) surface\textsuperscript{29,31} and increase the local surface density of states (LSDOS) at the Fermi level $E_F$, similar to what has been reported for Al and Ti caps on Cu films.\textsuperscript{38,39} That is, the Ti adatoms, which develop into a continuous cap layer, disturb the flat surface potential and also cause local surface states that electrons scatter into, both causing a decrease in the surface scattering specularly $p$. This is illustrated with the right
reported for Al on Cu, and has been attributed to the increasing y-axis in Fig. 1, which indicates the change in specularity \( \Delta p \) corresponding to the plotted \( \Delta R_s \). \( \Delta p \) is determined using the approximate form of the FS model for distinct top and bottom surfaces,\(^6\) a literature value for the average Co bulk in-plane resistivity \( \rho_0 = 5.6 \mu \Omega \) cm,\(^{42}\) a room temperature mean free path \( \lambda = 19.5 \) nm,\(^{23}\) and the nominal Co film thickness of 7.6 nm. We note that the approximate FS model for the \( d/\lambda \) ratio in our experiments causes a systematic error in \( \Delta p \) of 8%\(^6\), but this approximation is chosen here because it leads to a linear relationship between \( \Delta R_s \) and \( \Delta p \) and therefore allows us to indicate \( \Delta p \) directly as the right y-axis. All \( \Delta p \) values are negative, indicating a decrease in specularity by 0.07–0.14 upon the addition of a Ti cap. This suggests that the Co–vacuum interface specularity, which we have previously reported to be \( \rho = 0.55 \),\(^{33}\) is reduced to a partial specularity of \( \rho = 0.4–0.5 \) for the Co–Ti interface. This is distinctly different from the previously investigated interfaces of Cu with Ti,\(^{34,35}\) Al,\(^{36}\) and Ta,\(^{37}\) which all exhibit \( p = 0 \) after deposition of a Ti, Al, or Ta cap layer with \( d_{\text{cap}} > 0.16 \) nm, 1.4 nm, or 0.3 nm, respectively. We attribute the finite scattering specularity of the Co–Ti interface to their similar structure, which is also evidenced by their relatively high solubility\(^{31}\) and is expected to facilitate the epitaxial growth of the thin Ti cap, leading to a smooth coherent interface with partially specular electron scattering, as previously simulated for coated Cu surfaces with smooth and coherent interfaces.\(^{38,39}\) Similarly, partially specular scattering has been reported for the coherent Cu–Ni interface,\(^{40}\) where Cu and Ni also have a similar structure and are miscible.

The plot in Fig. 1 shows that TiN caps on Co(0001) also cause a resistance increase, with \( \Delta R_s = 1.9 \pm 0.3, 2.2 \pm 0.3, 2.7 \pm 0.5, 4.1 \pm 0.3, \) and \( 5.0 \pm 0.2 \) \( \Omega/\square \) for \( d_{\text{TiN}} = 0.0075, 0.015, 0.031, 0.063, \) and 0.13 nm, respectively. This increase up to \( d_{\text{TiN}} = 0.13 \) nm appears approximately linear on the semi-log plot and suggests a scattering specularity that decreases following approximately an exponential decay, similar to what has been reported for Al on Cu, and has been attributed to the increasing LSDOS\((E_f)\) with increasing Al cap thickness.\(^{31}\) Further increases in \( d_{\text{TiN}} \) yield no change in \( \Delta R_s = 4.9 \pm 0.4, 4.9 \pm 0.6, 4.9 \pm 0.6, \) and \( 4.7 \pm 0.2 \) \( \Omega/\square \) for \( d_{\text{TiN}} = 0.25, 0.50, 1.0, \) and 2.0 nm. This \( \Delta R_s \) corresponds to \( \Delta p = 0.51 \), which nearly matches the magnitude of the reported \( p = 0.55 \) for the bare Co surface, suggesting that the TiN deposition causes the Co surface to scatter completely diffuse (\( p = 0 \)) for \( d_{\text{TiN}} \geq 0.13 \) nm. The decrease in specularity is attributed to the perturbation of the smooth Co(0001) surface and the development of local surface states, which is the same argument as for the Ti caps. However, the final resistance and specularity are quite different for the Ti and TiN caps, with \( p = 0.4–0.5 \) for the Co–Ti interface but \( p = 0 \) for the Co–TiN interface.

Figure 2 shows representative curves indicating the change in sheet resistance \( \Delta R_s \) during in situ exposure to an increasing oxygen exposure.
O₂ partial pressure, from nominally 7.6-nm-thick epitaxial Co(0001) with Ti and TiN caps. The x-axis indicates the total oxygen exposure ΦO₂ over five orders of magnitude, from 0.5 Pa s to 10⁷ Pa s. The black curve in Fig. 2(a) is from the uncoated Co sample, showing a continuous resistance increase with increasing ΦO₂. ∆Rs increases approximately logarithmically up to ∆Rs = 0.40 Ω/Δ at ΦO₂ ≈ 10 Pa s, followed by a steep increase to 1.90 Ω/Δ approximately logarithmically up to a continuous resistance increase with increasing Φ. A similar experiment with Cu(001), which shows a peak in ΔRs at 1.3 Pa s that is attributed to the adsorption of a partial molecular oxygen monolayer, and a steep increase between 2 × 10⁵ Pa s and 2 × 10⁶ Pa s due to chemical oxidation of the Cu surface. 2 Similarly, we attribute the rapid resistance increase shown in Fig. 2 for Co to chemical surface oxidation, which, however, occurs at an exposure ΦO₂ = 10–50 Pa s that is approximately two orders of magnitude smaller than for Cu and is likely associated with the higher reactivity of Co and the associated lower (more negative) oxide formation enthalpy. 3 Correspondingly, the monolayer adsorption peak and valley cannot be observed for Co because of the early onset of the resistance increase due to chemical oxidation, which dominates over the resistance decrease expected for the formation of an adsorbed oxygen monolayer. The blue curve in Fig. 2(a) from a Co layer coated with 0.13 nm Ti exhibits a constant ∆Rs for ΦO₂ < 4 Pa s, a small local maximum of 0.08 Ω/Δ at 7 Pa s, and a minimum of −0.05 Ω/Δ at 27 Pa s followed by a rapid increase between 30 Pa s and 600 Pa s to a final ∆Rs = 2.73 Ω/Δ at ΦO₂ = 1 × 10⁵ Pa s. The steep increase is attributed to chemical oxidation of the Co surface, which is initially suppressed by oxidation of the reactive Ti and therefore occurs at nearly an order of magnitude higher ΦO₂ than for the pristine Co sample. This shift of the Co chemical oxidation to a larger exposure allows observation of a clear but small peak and valley in ∆Rs at 7 Pa s and 27 Pa s, which are attributed to the perturbation of the surface potential by a partial and then complete adsorbed oxygen monolayer on both the Ti cap as well as fractions of the Co surface that are not covered with Ti adatoms, qualitatively matching what has previously been reported for Cu(001). 3,11 We note that the negative ∆Rs is not only facilitated by a smooth surface potential of the adsorbed oxygen but also by chemical oxidation of the Ti, which converts from a metal to a dielectric, reducing the LSDOS at E_F and promoting more specular scattering at the Co surface, similar to what has been shown for Ti deposited on Cu. 24 The green curve from the dTi = 0.25 nm sample is qualitatively identical to the dTi = 0.13 nm curve. However, the increase due to Co oxidation is delayed by another two orders of magnitude to 10⁴–10⁵ Pa s, and the region with a negative ∆Rs is much more pronounced, showing a minimum ∆Rs = −0.26 Ω/Δ at 700 Pa s. Both of these effects are attributed to the greater effective thickness and the corresponding surface coverage of the dTi = 0.25 nm sample. More specifically, the additional Ti increases the time for oxidation and therefore delays Co oxidation. It also results in a larger coverage of Co by dielectric TiO₂, which facilitates specular scattering at the Co surface and therefore a negative ∆Rs. The red curve in Fig. 2(a) from a Co sample capped with 2.0 nm Ti shows a ∆Rs that remains nearly constant over the entire exposure range. The absence of an increase in ∆Rs indicates a negligible Co oxidation effect, which is attributed to the 2-nm-thick Ti forming a continuous and protective layer on the Co. The slight dip at 12 Pa s may be associated with oxygen adsorption, which temporarily smoothens the atomic level roughness of the Ti surface, while the gentle decrease around 10⁶ Pa s is an experimental artifact due to a slight decrease in sample temperature after Ti deposition, as confirmed with reference samples.

Figure 2(b) shows the corresponding plot for the resistance change during oxygen exposure of Co layers coated with TiN caps. The black line is the curve from the uncoated Co sample, which is already shown in Fig. 2(a) but is replicated here to facilitate easier comparison. The dark blue line is from a sample with a dTiN = 0.015 nm thick TiN cap layer, corresponding to just 7% of a TiN monolayer. It is qualitatively similar to the bare Co curve, showing a continuous increase in ∆Rs, with the steepest slope (in this semi-log plot) at around ΦO₂ = 10 Pa s. This value is comparable to the 10–50 Pa s range for the bare Co, indicating that the steep increase is attributed to oxidation of the Co surface that is not covered by the 7% monolayer TiN cap. Overall, this sample shows a slower resistance increase than the bare Co sample, indicating that even 7% of a TiN monolayer provides some oxidation protection. However, at large exposures, ∆Rs continues to increase to reach 3.35 Ω/Δ at 1 × 10⁷ Pa s, which is larger than for the bare Co sample. This difference may be due to experimental variations but may also indicate that a surface with oxidized TiN causes more diffuse electron scattering than a bare oxidized Co surface, similar to the dTi = 0.13 nm curve in Fig. 2(a), which is slightly above the dTi = 0 nm curve for large ΦO₂. The dark green curve in Fig. 2(b) from a sample with a 0.13 nm TiN cap shows only a small increase in ∆Rs to 0.50 Ω/Δ for ΦO₂ = 10⁷ Pa s, indicating that even this approximately 0.6 monolayer coating already provides substantial oxidation protection. This protection becomes complete for larger dTiN, as indicated by the dark red line in Fig. 2(b) for dTiN = 1 nm, which shows negligible variations in ∆Rs except for a slight decrease due to the same temperature effect as discussed above for the dTi = 2.0 nm sample.

Figure 3(a) shows the change in sheet resistance ∆Rs due to oxygen exposure of 7.6-nm-thick Co(0001) films with Ti or TiN cap layers vs their cap thickness. Each data point is obtained from one specific sample by taking the difference in the sheet resistance measured after removal from the vacuum system minus that measured in situ after cap layer deposition but prior to O₂ exposure. Here, the O₂ exposure includes both the in situ exposure to a 90% Ar–10% O₂ gas mixture with increasing pressure to 400 Pa as well as the exposure to atmospheric pressure air for approximately 10 min, yielding a total O₂ exposure of ~10⁶ Pa s. The first data point at dcap = 0 nm indicates the resistance change ∆Rs = 3.29 ± 0.23 Ω/Δ due to oxidation of the bare Co layer. This value is larger than ∆Rs = 2.61 Ω/Δ for ΦO₂ = 1 × 10⁶ Pa s presented in Fig. 2 for the same sample, indicating that the resistance of the bare Co sample continues to increase as the sample is exposed to atmospheric pressure air. We note, however, that a fraction of this difference may also be due to the experimental uncertainty of ±0.2 Ω/Δ since the in situ and ex situ sheet resistances are measured with two distinct experimental setups. The positive ∆Rs is attributed to the chemical oxidation of the Co surface, as mentioned above, resulting in (1) atomic-scale roughening of the conductive Co, which causes diffuse electron scattering and (2) consumption of some metallic Co by the developing oxide layer, effectively reducing the conductive cross sectional area. 3 In order to quantitatively determine the magnitude of the second effect, we measure the Co
oxide thickness by XRR and determine the loss of metallic Co to the oxide as we have previously described in Ref. 33. This analysis indicates that the majority (50%–80%) of the resistance increase can be attributed to the loss of metallic Co and that the measured $\Delta R_s$ corresponds to a change in resistivity $\Delta \rho = 0.84 \,\mu \Omega \cdot cm$ with a corresponding change in the surface scattering specularity $\Delta p = -0.1$. This specularity decrease is smaller than $\Delta p = -0.55$ that we have previously reported for the Co(0001) surface oxidation in air. We do not know the exact cause for this difference but speculate that the controlled low-pressure oxidation in the argon–oxygen mixture may result in a smoother (less defect containing) metal–oxide interface than during a (humid) air exposure, leading to partially specular scattering at the interface between Co and Co-oxide in this study. We note that the measured $\Delta p$ has a relatively large experimental uncertainty due to the time delay between transport measurements and the oxide quantification by XRR and also note that no systematic difference in the interface between the Co film and its oxide could be detected by XRR between dry-O$_2$ and air exposed samples, which both exhibit root-mean-square roughnesses of 0.3–0.4 nm.

The Co film coated with 0.13 nm of Ti yields $\Delta R_s = 3.61 \pm 0.75 \,\Omega/\ell$, which, within uncertainty, is equal to that of bare Co, confirming that the partial coverage of $d_{Ti} = 0.13$ nm is not sufficient to inhibit Co oxidation. $\Delta R_s$ decreases to $1.87 \pm 0.70 \,\Omega/\ell$ for $d_{Ti} = 0.25$ nm, indicating partial oxidation protection by the Ti cap, and drops to approximately zero for $d_{Ti} = 0.50$ nm, 1.0 nm, and 2.0 nm with measured values of $\Delta R_s = -0.20 \pm 0.18 \,\Omega/\ell$, $-0.18 \pm 0.20 \,\Omega/\ell$, and $-0.12 \pm 0.30 \,\Omega/\ell$. Thus, Ti capping layers with $d_{Ti} \geq 0.5$ nm completely suppress the resistance increase associated with Co oxidation, indicating that these caps are likely continuous layers. We note that these $\Delta R_s$ values are even slightly negative, suggesting that the Ti oxidation may result in a Co–TiO$_2$ metal–dielectric interface, which facilitates specular electron scattering. This interpretation is consistent with previous reports on a resistance decrease during oxidation of Cu layers that were coated with 0.4 nm of Al$^{31}$ or 0.6 nm of Ti$^{32}$.

Figure 3(a) also shows the measured $\Delta R_s$ for Co coated with TiN. It is $4.46 \pm 0.35$, $3.95 \pm 0.27$, $4.51 \pm 0.38$, and $3.15 \pm 0.29 \,\Omega/\ell$ for $d_{TiN} = 0.0075$, $0.015$, $0.031$, and $0.063$ nm, corresponding to an average $\Delta R_s = 4.02 \,\Omega/\ell$ in this thickness range. This is 22% larger than $\Delta R_s = 3.29 \,\Omega/\ell$ for bare Co, suggesting that sub-0.1-nm-thick TiN capping layers may exacerbate the roughening and/or the specularity loss at the Co surface upon oxidation. The plotted $\Delta R_s$ drops to approximately zero for $d_{TiN} \geq 0.13$ nm with measured $\Delta R_s = 0.26 \pm 0.24$, $0.32 \pm 0.42$, $0.34 \pm 0.76$, and $0.11 \pm 0.99 \,\Omega/\ell$ for $d_{TiN} = 0.13$, $0.25$, $0.50$, and 1.0 nm. That is, TiN forms a protective capping layer even if its nominal thickness is only 0.13 nm, which is below ~0.2 nm for a TiN monolayer. This may be attributed to an overstoichiometric N-to-Ti ratio in the Ti cap such that the excess adsorbed surface nitrogen$^{37,48}$ blocks Co oxidation.

Figure 3(b) shows a similar plot of the change in sheet resistance vs cap layer thickness. However, contrary to Fig. 3(a), the plotted $\Delta R_s$ includes here the resistance change due to both cap layer deposition and oxygen exposure. That is, the data points represent the difference between the resistance measured after air exposure minus the in situ $R_s$, prior to the deposition of a cap layer. Thus, they correspond to the sum of the values plotted in Figs. 1 and 3(a). The data point for the bare Co sample ($d_{cap} = 0$ nm) is identical to that shown in Fig. 3(a) since the pre-cap and post-cap $R_s$ values are identical in the absence of a capping layer. In contrast, $d_{Ti} = 0.13$ nm and 0.25 nm result in larger $\Delta R_s$ values than in Fig. 3(a) because the deposition of the Ti cap causes a resistance increase prior to oxygen exposure. Larger Ti cap thicknesses result in a relatively small $\Delta R_s \sim 1 \,\Omega/\ell$ for $d_{Ti} \geq 0.5$ nm. This is due to the effective suppression of Co oxidation by the Ti layer such that the $\Delta R_s$ value approximately matches the values in Fig. 1. The data for the Co films coated with TiN cap layers qualitatively resemble those for the Ti coatings. They show the largest $\Delta R_s$ for small $d_{TiN} \leq 0.063$ nm and a drop to an approximately constant $\Delta R_s \sim 5 \,\Omega/\ell$ for $d_{TiN} \geq 0.13$ nm, which is attributed to the suppression of Co oxidation. However, 5 $\,\Omega/\ell$ for the TiN caps is considerably larger than 1 $\,\Omega/\ell$ for the Ti caps, which is attributed to the larger reduction in scattering specularity for the TiN vs the Ti coatings, as discussed above and shown in Fig. 1. This suggests that Ti is the more promising barrier material than TiN for Co metallization, if considering only the resistivity benefit.
IV. CONCLUSIONS

7.6-nm-thick epitaxial Co(0001) samples were sputter deposited onto c-plane sapphire substrates and coated in situ with either Ti or TiN capping layers with thicknesses ranging from 0 nm to 2.0 nm. The change in sheet resistance resulting from oxidation of the Co(0001) surface and/or the capping layers was measured in real time using in situ measurements performed as a function of oxygen exposure. The uncoated Co surface readily oxidizes upon \( \text{O}_2 \) exposure, leading to a resistance increase that this attributed to a drop in the electron surface scattering specularity and an effective decrease in the film thickness due to Co consumption by the developing surface oxide. Ti cap layers with \( d_{\text{Ti}} \geq 0.5 \text{ nm} \) protect the Co from oxidation and promote a relatively high conductance, which is attributed to partially specular (\( p = 0.4–0.5 \)) electron scattering at the Co–Ti interface, which does not decrease upon oxygen exposure. TiN cap layers also protect Co from oxidation, even for very thin \( d_{\text{TiN}} \leq 0.13 \text{ nm} \). However, the resistance is considerably higher than for the Ti caps, which is attributed to completely diffuse electron scattering at the Co–TiN interface. Consequently, TiN represents a more promising liner/barrier material than TiN for low resistance Co interconnects, as long as the Ti barrier is thick \( d_{\text{Ti}} \geq 0.5 \text{ nm} \) for our processing conditions) to suppress Co oxidation.

We note that our results confirm previous studies, suggesting that both cap layers \(^{27,28,89} \) and surface oxidation \(^{29–29} \) can strongly affect the surface scattering specularity. However, the approximately four times larger resistivity increase due to TiN vs Ti caps is unexpected. More specifically, previous studies on the effect of Ti and Al caps on Cu layers attribute the resistivity increase to a transition to diffuse scattering, which is facilitated by a large density of states in the cap material. Based on these studies, Ti with larger density of states than TiN is expected to cause more diffuse electron scattering, which is opposite to the observed effect. The reasons for this difference are not clear, but may be related to an epitaxial growth of hexagonal Ti on hexagonal Co, leading to a partial matching of the Co and Ti Fermi surfaces, which effectively extends coherent electron transport from the Co into the Ti and, in turn, facilitates specular scattering at the Ti-coated Co surface.

ACKNOWLEDGMENTS

The authors acknowledge funding from SRC under Grant Nos. 2966 and 2881, the NY State Empire State Development’s Division of Science, Technology and Innovation (NYSTAR) through Focus Center-NY–RPI Contract No. C150117, and the NSF under Grant Nos. 1740271 and 1712752.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

REFERENCES