Resistivity scaling in epitaxial CuAl$_2$(001) layers

Minghua Zhang and Daniel Gall

Abstract—Epitaxial CuAl$_2$(001) layers with thickness $d = 10.2 - 141$ nm are deposited by co-sputtering onto MgO(001) substrates at 300 °C and their resistivity $\rho$ is measured in situ to quantify the CuAl$_2$ resistivity scaling. A combination of X-ray diffraction $\theta$-2$\theta$ scans, $\omega$ rocking curves and $\phi$-scans confirm the single crystal microstructure with a 45°-rotated epitaxy with CuAl$_2$(001) $\parallel$ MgO(001) and CuAl$_2$(100) $\parallel$ MgO(110). The measured $\rho$ increases with decreasing $d$, which is well described by the Fuchs-Sondheimer model, yielding a room-temperature electron mean free path $\lambda = 15.6$ nm with a bulk resistivity $\rho_o = 7.7 \mu\Omega$ cm. The latter value is 18% above the previously reported $\rho_o$, which is attributed to electron scattering at Al vacancies with a concentration of 6.4% per site, as quantified by Rutherford back scattering and X-ray reflectivity. Transport measurements at 77 K confirm that $\rho_o \lambda = (12 \pm 1) \times 10^{-16}$ $\Omega$m$^2$ is temperature-independent. This value is 79% larger than for Cu, indicating a more pronounced resistivity size effect in CuAl$_2$. Thus, CuAl$_2$ is only promising as Cu-replacement interconnect metal if its low melting point facilitates large grains and its high cohesive energy provides reliability benefits and an associated reduction in liner thickness.

Index Terms—Cu replacement, interconnects, mean free path, resistivity scaling, CuAl$_2$, surface scattering.

I. INTRODUCTION

Downscaling of conventional Cu interconnects in integrated circuits represents a major challenge because the resistivity increases steeply as the half-pitch is reduced to below the electron mean free path, causing an increasing resistance-capacitance delay [1]-[4]. The resistivity increase in narrow metal lines is primarily due to electron scattering at surfaces and grain boundaries, and is typically described by the Fuchs and Sondheimer (FS) [5], [6] and the Mayadas and Shatzkes (MS) [7] models, respectively. These models suggest that a conductor with a reasonably small bulk resistivity $\rho_o$ and a small bulk electron mean free path $\lambda$ may exhibit a higher conductivity than Cu in the limit of narrow wires, if the product $\rho_o \lambda$ of this conductor is smaller than for Cu [8], [9]. The search for possible Cu replacement materials has initially focused on elemental metals like Co [10], Ru [11], [12], and W [13], with Ru exhibiting a particularly promising combination of low resistivity and excellent reliability for sub-5 nm interconnects [14]-[16]. More recent research includes low-resistivity binary and ternary compounds which exhibit a high cohesive energy and therefore promise a high reliability as potential interconnect conductor [17]. This includes transition metal aluminides and especially CuAl$_2$, which has a good expected resistivity scaling and favorable wetting properties [18], [19]. Additionally, reported capacitance-voltage (C-V) tests and time-dependent-dielectric-breakdown (TDDB) evaluations of CuAl$_2$ on thermal-SiO$_2$/p-Si substrates indicate good reliability in comparison to conventional Cu/TaN structures [20], suggesting that CuAl$_2$ may facilitate reduced liner/barrier widths or even barrierless CuAl$_2$ interconnects, with a corresponding conductance benefit. On the other hand, open questions remain regarding the effects of the CuAl$_2$ crystallinity and grain structure, surface oxidation, and deviations from stoichiometry on the CuAl$_2$ line resistivity and reliability. Most importantly, the intrinsic resistivity size effect in CuAl$_2$ is not established yet, which motivates our study on the electron transport in thin epitaxial CuAl$_2$ layers.

In this paper, we report on the resistivity scaling in CuAl$_2$ (Fm$\overline{3}$m) as measured using epitaxial CuAl$_2$(001)/MgO(001) layers. Epitaxial single-crystal layers are used because the absence of grain boundaries eliminates the confounding effects from electron grain boundary scattering and facilitates direct quantification of the electron mean free path which is the primary metric used to quantify the resistivity size effect. We use in situ transport measurements to avoid possible effects of surface oxidation on the resistivity and possible Al segregation induced by the oxidation. We determine $\lambda = 15.6$ nm by fitting the measured $\rho$ vs layer thickness $d$ with the classical FS model [5], [6]. The corresponding $\rho_o \lambda = (12 \pm 1) \times 10^{-16}$ $\Omega$m$^2$ is temperature independent, as confirmed by measurements at 77 K, and is 28% larger than the prediction of 9.34 $\times 10^{-16}$ $\Omega$m$^2$ from first-principles calculations [21]. Thus, CuAl$_2$ exhibits a slightly larger resistivity size effect than Cu and is therefore only promising as future interconnect metal if it facilitates elimination or a thickness reduction of the liner.

II. PROCEDURE

CuAl$_2$ thin films were deposited in a three-chamber ultra-high vacuum DC magnetron sputtering system with a base pressure $< 10^{-9}$ Torr [22]. Polished 1×1 cm$^2$ MgO(001) substrates were cleaned in sequential ultrasonic baths [23] and degassed in vacuum at 1000 °C for 1 hour. Subsequent depositions were done in 3 mTorr 99.9999% pure Ar, using constant powers of 120 and 30 W applied to 5-cm-diameter 99.9995 % Al and 99.999 % Cu targets which were facing the substrate at -45 and +45 tilts, yielding a deposition rate of 0.24

The authors are with the Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, 110 8th St, Troy, NY 12180, USA. Corresponding author: Daniel Gall; email: galld@rpi.edu

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nm/s. The substrates were continuously rotated to maximize compositional uniformity and were kept at 300 °C which was the optimal temperature to facilitate epitaxial layer growth, good crystalline quality, low surface roughness, and negligible secondary phase formation. The deposition time was adjusted to obtain a series of CuAl₂ films with thickness \( d = 10.2 - 141 \) nm, as measured by X-ray reflectivity (XRR) for \( d < 100 \) nm. The thickness of thicker samples was determined from the deposition rate measured from thinner samples because no XRR oscillations can be resolved for \( d > 100 \) nm. After cooling down to room temperature, the samples were transferred in vacuum to the analysis chamber for \textit{in situ} resistivity measurements using a linear four-point probe with a 1 mm inter-probe spacing. For each sample, five measurements with different currents ranging from 1-100 mA were performed and the resistivity was determined from the fitted voltage-vs-current slope.

X-ray diffraction (XRD) and XRR measurements were done in a Panalytical X’pert PRO MPD system with a Cu Kα source using a 45 kV accelerating voltage and a 40 mA current. Symmetric \( \theta \)-2\( \theta \) scans were obtained using a parallel beam geometry with an X-ray mirror and a PIXcel solid-state line detector with a 0.165 mm active length acting as a point detector. \( \omega \) rocking curves were obtained with the same optics. Azimuthal \( \phi \)-scans were obtained at constant \( \chi \) and 2\( \theta \) angles using a point source in combination with an X-ray lens yielding a quasi-parallel beam with an equatorial and axial divergence of 0.3°. Rutherford Backscattering Spectrometry (RBS) was conducted using a linear Dynamitron ion accelerator providing a 2 MeV \( ^4 \)He\(^+ \) ion beam. Backscattered particles were collected with a Si surface barrier detector at a scattering angle of 166°. The Cu and Al atomic areal densities were obtained from RBS spectra using the SIMNRA simulation software [24].

III. RESULTS AND DISCUSSION

Figure 1(a) shows XRR results from a nominally 72-nm-thick CuAl₂(001)/MgO(001) layer. The measured intensity is plotted as solid line in a logarithmic scale as a function of the scattering angle 2\( \theta \). Data fitting yields the dotted line which is offset by a factor of 0.2 for clarity purposes. It describes the measured data well and corresponds to a 69.8-nm-thick CuAl₂ layer. The measured backscattered intensity vs particle energy is plotted as brown stars and the green curve is the result of XRR oscillations. The measured intensity is converted into a consumed CuAl₂ thickness of 2.5 ± 0.7 nm, yielding an as-deposited \( d_a = 72.3 ± 0.9 \) nm, consistent with the 3.3-nm-thick surface oxide measured by XRR. We note that the high vapor mean-square (RMS) roughness of 0.7 ± 0.2 nm for the top surface, 0.4 ± 0.1 nm for the oxide-CuAl₂ interface, and 1.5 ± 0.3 nm for the interface between the CuAl₂ layer and the MgO(001) substrate, suggesting negligible chemical reaction at the layer-substrate interface. Similar XRR measurements and analyses are performed for all samples. The resulting thickness values for as-deposited and air exposed layers are listed in Table I and are used below to determine the \textit{in situ} and \textit{ex situ} resistivity, respectively.

Figure 1(b) shows a typical RBS spectrum from the same sample. The measured backscattered intensity vs particle energy is plotted as brown stars and the green curve is the result from curve fitting. The areas under the measured peaks yield total area-densities of Cu and Al atoms of (1.55 ± 0.05) and (2.77 ± 0.09) \( \times 10^{17} \) atoms/cm\(^2\), indicating a composition with 36 % Cu and 64 % Al which is close to the stoichiometric 33% Cu and 67% Al. We note that a defect-free fully dense stoichiometric CuAl₂ layer with a thickness of 72.3 nm (as determined by XRR) has expected Cu and Al atomic densities of (1.50 ± 0.02) and (3.01 ± 0.04) \( \times 10^{17} \) atoms/cm\(^2\), respectively. The measured values are 3.2% above and 8.0% below these expected densities, indicating a 3.2% excess of Cu atoms which may form anti-site defects and occupy 1.6% of the Al-sites. Conversely, the 8.0% deficiency in Al atoms yields a 6.4% vacancy density on Al-sites. The spectrum in Fig. 1(b) also has a small peak at 0.69 MeV which is attributed to surface oxygen. Curve fitting indicates (2.4 ± 0.9) \( \times 10^{16} \) oxygen atoms/cm\(^2\) which corresponds to a stoichiometric oxide thickness of 3.4 ± 1.0 nm, consistent with the 3.3-nm-thick surface oxide measured by XRR. We note that the high vapor...
pressure of Al makes deposition of stoichiometric CuAl₂ challenging as a fraction of deposited Al atoms evaporate at the 300 °C deposition temperature. In addition, previous studies [18], [27] suggest that Al diffusion in aluminide intermetallic compounds facilitates Al surface segregation, preferential Al surface oxidation and a resulting change in composition during air exposure.

Figure 2 shows representative XRD results from the same 69.8-nm-thick CuAl₂(001) layer used for Fig. 1. The θ-2θ pattern in Fig. 1(a) shows a strong doublet feature at 42.92° and 43.04° from MgO 002 substrate reflections of the Cu Kα₁ and Kα₂ x-rays and layer peaks at θ = 15.59° and 31.57° that are ascribed to the CuAl₂ 001 and 002 reflections. These peaks confirm the formation of the ordered CuAl₂ compound and indicate a measured out-of-plane lattice constant of 5.67 Å. This value is 1.8% smaller than the reported 5.77 Å [28], which may be attributed to deviations from stoichiometry (in particular Al vacancies) and/or an in-plane biaxial tensile stress caused by the lattice mismatch with the MgO substrate or differential thermal contraction after deposition as the expansion coefficients are 1.3 × 10⁻⁵ K⁻¹ for MgO [29] and 2.0 × 10⁻⁵ K⁻¹ for CuAl₂ [30]. We note that the CuAl₂ 001 reflection is forbidden for the perfect stoichiometric CuAl₂ lattice, indicating a considerable point-defect concentration in our samples which breaks the translational symmetry, consistent with the RBS compositional analysis which indicates Al vacancies. The CuAl₂ 004 reflection is expected at 2θ = 64.83° but is too weak to be detected for all layers and is therefore not included in Figure 2(a). No other peaks can be detected over the entire measured 2θ = 10–80° range, indicating a CuAl₂ 001 orientation along the growth direction without detectable misoriented grains or secondary phases.

<table>
<thead>
<tr>
<th>d [μm]</th>
<th>ρ [μΩ cm]</th>
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<tr>
<td>6.0</td>
<td>24.3</td>
</tr>
<tr>
<td>9.0</td>
<td>20.2</td>
</tr>
<tr>
<td>12.0</td>
<td>17.1</td>
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<tr>
<td>15.0</td>
<td>14.0</td>
</tr>
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</table>

Table Ⅰ also includes the resistivity measured ex situ, that is, after exposure to air. The ex situ values are 6-13% larger than the in situ resistivity for all layers. This increase is most pronounced for the thinnest layers, suggesting that the effect from air exposure is primarily a surface effect. Similar resistance increases during air exposure have been previously reported for multiple metals including Cu [32], [33], Co [10], [34], Ni [35], Ag [36], and Nb [37] and have been attributed to a surface potential perturbation which causes more diffuse electron scattering. In contrast, the resistivity of more electronegative metals including Ru [11], Rh [38], [39], Ir [40], and W [41] is less affected by air exposure [42]. Similarly, we attribute the resistivity increase during air exposure of our CuAl₂ layers to an increase in diffuse electron surface scattering and note that air exposure also causes a 3-10% reduction in the conductive cross-sectional area of the layers since a fraction of the metal is consumed by the growing surface oxide, as quantified by XRR measurements. The latter causes an increase in the measured ex situ sheet resistance but does not contribute to the listed resistivity increase because the in situ and ex situ resistivities in Table I are determined using the as-deposited and measured layer thicknesses, respectively. Nevertheless, in the following, we use primarily the in situ resistivity values to quantify the intrinsic CuAl₂ resistivity size effect since the...
resistivity of air exposed samples may also be affected by surface oxidation induced segregation [43] and roughness [44].

The CuAl2(001) resistivity at 77 K is plotted in Fig. 3 as blue triangles. It exhibits a similar increase with decreasing thickness, from ρ = 2.2 ± 0.1 μΩ cm for d = 141 nm to 7.1 ± 0.4 μΩ cm for d = 9.2 nm. The low-temperature values are 5.5-6.0 μΩ cm below those at room temperature. This difference is (within experimental uncertainty) independent of d and is attributed to an approximately additive resistivity contribution from electron-phonon scattering. We note that the smaller bulk resistivity at 77 K results in a larger relative resistivity size effect. More specifically, the room-temperature resistivity increases by 69% as d is reduced from 141 to 10.2 nm, while the corresponding increase is 223% at 77 K.

The solid lines through the data points are the result from curve fitting using the integral form of the FS model [5], [6]. This is done by setting the specularity parameters p1 and p2 for both the top surface and bottom MgO-CuAl2 interfaces to zero. This approach has previously been applied to quantify the resistivity size effect in epitaxial Ir [40], Rh [38], Co [10], Ru [11], and Ti3SiC2 [45] layers and yields a λ value which can be understood as an upper bound to possible λ-values or alternatively as the bulk electron mean free path for the case of completely diffuse surface scattering. Data fitting of the room temperature resistivity yields a bulk resistivity ρ0 = 7.7 ± 0.2 μΩ cm and λ = 15.6 ± 1.2 nm. Correspondingly, analysis of the low temperature data yields ρ0 = 2.1 ± 0.1 μΩ cm and λ = 59 ± 4 nm at 77 K. The corresponding product ρλ = (11.9 ± 1.0) and (12.9 ± 1.0) × 10^{-16} Ωm^2 at 295 and 77 K, respectively. These two values are identical within experimental uncertainty, suggesting that ρλ is temperature independent, as expected from classical transport models [8]. We use in the following and in the abstract a rounded value ρλ = 12 × 10^{-16} Ωm^2, where the significant figures indicate the ± 1 uncertainty. This ρλ value is 28 % larger than the previously predicted ρλ = 9.34 × 10^{-16} Ωm^2 from first-principles calculations [21]. This deviation is relatively small and within the typical range (25-45%) of many metals which show considerably larger effective electron mean free paths from measured ρ vs d data than from first-principles calculations [8]. The larger experimental λ values in comparison to first-principles predictions have previously been attributed to experimental roughness [41], [44], misfit dislocations at the MgO-layer interface that increase the measured effective mean free path, anisotropy in the electron-phonon scattering cross sections [8], or the breakdown of the classical FS model at small dimensions [46].

Our measured ρλ = 12 × 10^{-16} Ωm^2 for CuAl2 is 79 % and 135 % larger than for Cu [2] and Ru [11], respectively, and comparable to ρλ values for Co [10] and W [13]. Thus, CuAl2 does not provide an intrinsic conductance advantage in comparison to other metals for narrow interconnects. Nevertheless, CuAl2 exhibits some key advantages: (1) CuAl2 has a considerably lower melting point Tm = 592 °C [47] than competing metals like Cu, W, Ru and Co with Tm > 1000 °C. The low melting point facilitates CuAl2 grain growth during annealing at back-end-of-line compatible temperatures. This, in turn, results in an expected CuAl2 conductance benefit as competing metals exhibit substantial resistance contributions from electron scattering at grain boundaries [2], [8], [48], [49]. (2) CuAl2 has a higher cohesive energy than Cu [19] and therefore a higher expected resistance against electromigration and diffusion into the dielectric, and possibly also against oxidation during typical 400 °C back-end-of-line annealing steps. Thus, CuAl2 shows promise as a potential liner-free interconnect metal with the associated conductance benefits. This is supported by previously reported TDDB measurements which found a longer lifetime for CuAl2 in direct contact with SiO2 than for Cu with a TaN barrier layer [20].

![Resistivity ρ vs thickness d of epitaxial CuAl2(001) films measured in situ (in vacuum) at 295 K and in liquid N2 at 77 K.](https://dx.doi.org/10.1109/TED.2022.3188952)

![CuAl2(001)/MgO(001)](https://dx.doi.org/10.1109/TED.2022.3188952)

### Table I. Measured layer thickness d_{ox}, surface oxide thickness d_{ox}, as-deposited thickness d_{ox}, prior to air exposure, and resistivity measured in situ in vacuum and ex situ after air exposure at 295 K, and immersed in liquid N2 at 77 K, from epitaxial CuAl2(001)/MgO(001) layers.

<table>
<thead>
<tr>
<th>d_{ox} (nm)</th>
<th>d_{ox} (nm)</th>
<th>d_{ox} (nm)</th>
<th>ρ (μΩ cm)</th>
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<tbody>
<tr>
<td>In situ</td>
<td>Ex situ</td>
<td>295 K</td>
<td>77 K</td>
</tr>
<tr>
<td>141 ± 4</td>
<td>—</td>
<td>7.9 ± 0.2</td>
<td>8.4 ± 0.2</td>
</tr>
<tr>
<td>69.8 ± 0.9</td>
<td>3.3</td>
<td>8.5 ± 0.2</td>
<td>9.3 ± 0.3</td>
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<tr>
<td>42.1 ± 0.5</td>
<td>2.3</td>
<td>8.7 ± 0.3</td>
<td>9.7 ± 0.3</td>
</tr>
<tr>
<td>21.1 ± 0.3</td>
<td>2.5</td>
<td>9.8 ± 0.3</td>
<td>10.5 ± 0.4</td>
</tr>
<tr>
<td>9.2 ± 0.2</td>
<td>1.4</td>
<td>10.2 ± 0.3</td>
<td>12.6 ± 0.4</td>
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### IV. CONCLUSIONS

CuAl2 layers that are sputter deposited onto MgO(001) substrates at 300 °C are epitaxial layers with CuAl2(001) || MgO(001) and CuAl2(100) || MgO(110), as determined by XRD. Compositional analyses by RBS in combination with XRR show that air exposure causes a 1.4-3.3 nm thick surface oxide. They also reveal an Al vacancy concentration of 6.4% per Al site. In situ transport measurements indicate a resistivity increase with decreasing layer thickness that is best described by a bulk electron mean free path λ = 15.6 nm with a bulk resistivity ρ0 = 7.7 μΩ cm. The corresponding values for electron transport at 77 K are λ = 59 nm and ρ0 = 2.1 μΩ cm, yielding an overall product ρλ = 12 × 10^{-16} Ωm^2 which is independent of temperature. The overall results suggest that CuAl2 has a more pronounced resistivity size effect than Cu and a comparable resistivity scaling as Co and W. Thus, CuAl2 is only promising as interconnect material if its high cohesive energy facilitates reduction or elimination of a liner/barrier layer.

References


