Resistivity size effect in epitaxial VNi₂ layers

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Epitaxial VNi₂ layers are deposited onto MgO(001) and their resistivity ρ measured as a function of layer thickness d = 10.5-138 nm to quantify the resistivity size effect. The layers exhibit resistivity minima at both a stoichiometric V:Ni = 1:2 composition and a 700 °C growth temperature, which is attributed to electron scattering at V-Ni antisite defects and is described using the ordering parameter within the framework by Rossiter. A cube-on-cube epitaxy of the fcc parent structure on MgO(001) leads to two possible layer orientations for orthorhombic VNi₂(010) and VNi₂(103), resulting in considerable atomic disorder at domain boundaries, consistent with relatively small x-ray coherence lengths of 8 and 14 nm in-plane and along the growth direction of a 33.5 nm thick layer. In situ ρ vs d measurements yield a bulk resistivity ρ₀ = 46 ± 2 μΩ cm and a benchmark quantity ρ₀λ = (160 ± 10) × 10⁻¹⁶ Ωm², where λ is the bulk electron mean free path. Air exposure causes a minor resistivity increase due to a 2 ± 1 nm thick surface oxide that perturbs the surface potential. Resistivities at 77 K are Δρ = 16 ± 3 μΩ cm below those at room temperature. This Δρ is thickness independent and is close to the previously predicted 13.9 μΩ cm bulk resistivity for VNi₂ along [100]. However, the measured bulk resistivity is well above this prediction, which is attributed to electron scattering at domain boundaries / atomic disorder. Consequently, the theoretically predicted superior directional conduction cannot be experimentally confirmed in this study. The overall results indicate that VNi₂ is only a promising compound for narrow interconnects if a synthesis scheme can be developed that results in strong atomic order, a negligible domain boundary density, and a [100] crystalline orientation along the transport direction.
I. INTRODUCTION

The electrical resistivity $\rho$ of metallic thin films or wires increases as their thickness or width decreases below the electron mean free path.\textsuperscript{1-3} This increase is referred to as the resistivity size effect and impedes the continued downscaling of devices in integrated circuits because of the resulting increase in power consumption and resistance-capacitance (RC) delays in the metal wires that interconnect transistors.\textsuperscript{4,5} Electron scattering at surfaces\textsuperscript{6-9} and grain boundaries\textsuperscript{10,11} are the main cause for the resistivity size effect, as described by the semiclassical Fuchs and Sondheimer (FS)\textsuperscript{12,13} and Mayadas and Shatzkes (MS)\textsuperscript{14} models, respectively. These models predict that both surface and grain boundary scattering result in a resistivity contribution that is proportional to the product of the bulk resistivity $\rho_o$ times the bulk electron mean free path $\lambda$.\textsuperscript{15} Consequently, the search for candidate materials that conduct well at small dimensions and are promising to replace the current copper interconnects focuses on metals with a small $\rho_o \lambda$ product.\textsuperscript{16-19} However, despite considerable research efforts, replacing Cu ($\rho_o \lambda = 6.7 \times 10^{-16} \ \Omega \text{m}^2$)\textsuperscript{20} with a reliable alternative conductor remains a major challenge.

Binary and ternary compounds have been proposed as a possible alternative conductor to replace elemental metals for highly scaled interconnects based on their promising $\rho_o \lambda$ descriptor,\textsuperscript{21} interdiffusion reliability\textsuperscript{22} and back-end-of-line-compatible growth temperature.\textsuperscript{23} Reports on intermetallic compounds including CuAl$_2$,\textsuperscript{24} NiAl,\textsuperscript{23} Cu$_2$Mg,\textsuperscript{25} and CuTi\textsuperscript{26} indicate a promising resistivity scaling that is comparable to elemental metals. They also exhibit good time-dependent dielectric breakdown reliability and electromigration properties.\textsuperscript{27,28} Layered MAX phase materials have even lower (below elemental metals) resistivity scaling for transport in the in-plane direction, which has been experimentally confirmed for Ti$_4$SiC$_3$\textsuperscript{29} and V$_2$AlC\textsuperscript{30} and is attributed to their predicted anisotropic Fermi surfaces.\textsuperscript{21,31} However, their bulk resistivities are likely too high to be competitive for interconnect applications.\textsuperscript{29} Recently, first-principles computational methods have revealed additional promising compounds with electron velocities that are concentrated near a single transport axis,
providing the possibility for wire conduction with minimal electron scattering at all four (top/bottom/left/right) surfaces of an interconnect line\textsuperscript{21,32} One of these promising compounds is VNi\textsubscript{2}, which has a calculated cohesive energy that is 1.5 times higher than that of Cu, and a low predicted effective $\rho_o\lambda = 4.5 \times 10^{-16}$ $\Omega$m\textsuperscript{2} along the [001] crystalline direction,\textsuperscript{21} suggesting that it would outperform both the stability and the conductivity of Cu for narrow interconnect lines. Relatively little is known about the VNi\textsubscript{2} compound, as previous studies have mainly focused on its thermodynamic and structural properties as well as its synthesis during high-temperature solidification.\textsuperscript{33,34} Thus, the experimental confirmation of its superior conduction at small dimensions and even a measurement of its bulk resistivity is still lacking. Therefore, the goal of the present study is to measure the resistivity of VNi\textsubscript{2} thin films and validate its low resistivity size effect.

In this article, we report on the resistivity scaling of the ordered intermetallic VNi\textsubscript{2} compound. Deposition conditions during co-sputtering are tuned to optimize composition, crystalline quality, phase purity, surface smoothness, and atomic ordering. We use \textit{in situ}, \textit{ex situ} and cryogenic transport measurements and determine $\rho_o = 46 \pm 2$ $\mu$Ω cm and $\lambda = 30 \pm 5$ nm at 293 K. The measured room temperature resistivity is three times higher than the previously predicted value along [100],\textsuperscript{21} which is ascribed to structural multiplicity. More specifically, two possible layer orientations VNi\textsubscript{2}(103) and VNi\textsubscript{2}(010) share the same atomic positions but different ordering of V and Ni atoms in a slightly distorted face-centered cubic (fcc) parent structure. X-ray diffraction cannot distinguish between the two structurally similar orientations. However, the deviation from long range atomic order causes extra electron scattering and a correspondingly high $\rho_o$. Thus, VNi\textsubscript{2} is a promising interconnect conductor only if future studies can achieve a single domain or even single crystal VNi\textsubscript{2} growth, and demonstrate the high conductivity along the [100] direction.

\section*{II. EXPERIMENTAL METHODS}

VNi\textsubscript{2} thin films were deposited onto MgO(001) in a three-chamber ultra-high
vacuum DC magnetron sputtering system with a base pressure < 10⁻⁹ Torr. Single-side polished 10 × 10 mm² MgO(001) substrates were cleaned in consecutive ultrasonic baths of trichloroethylene, acetone, iso-propyl alcohol, and de-ionized water, blown dry with dry N₂, mounted on a Mo sample holder, inserted into the deposition system through a load lock and degassed in vacuum at 1000 °C for 1 hour. Experiments using other substrates including A plane, C plane, and R plane Al₂O₃ yielded VNi₂ layers that exhibit multiple crystalline orientations. That is, they are polycrystalline and therefore less suited for the intended transport studies and, in turn, are not reported in this paper. 5-cm-diameter 99.9 % V and 99.99 % Ni targets facing the substrate at -45 and +45 tilts were sputter-cleaned for 5 min with a shutter covering the substrate prior to depositions in 3 mTorr 99.999% pure Ar, employing constant powers of 50 and 57 W applied to V and Ni sources to achieve a stoichiometric 1:2 deposition flux with a deposition rate of 0.11 nm/s. The substrates were continuously rotated to maximize compositional uniformity and were kept at 700 °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 VNi₂ films with thickness \( d = 10.5 - 138 \) nm, as measured by X-ray reflectivity (XRR). The thickness of the thickest \( d = 138 \) nm layer was determined from the deposition rate measured from thinner samples because no XRR oscillations can be resolved for approximately \( d > 100 \) nm. After cooling down to room temperature, the samples were transferred in vacuum to the analysis chamber for \textit{in situ} electrical transport measurements using a linear four-point probe with a 1 mm inter-probe spacing operated with 1-100 mA. Subsequently, samples were removed from the vacuum and submerged in liquid nitrogen to perform similar four-point probe measurements at 77 K, followed by \textit{ex situ} room temperature resistivity measurements after warming up by continuously blowing dry N₂ gas to the sample surface to minimize water condensation.

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 acquired 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°.

Photoelectron spectroscopy (XPS) analyses were performed using Al K\( \alpha \)
radiation (1486.6 eV) in a PHI 5000 Versaprobe system with a hemispherical analyzer
and an 8-channel detector. The sample surfaces were sputter etched using a 3 keV 2 mA
Ar\(^+\) beam incident at 45° relative to the surface normal over a 1 mm\(^2\) area, yielding a 7
nm/min sputter rate. Ion beam sputtering was done in 15 s steps, corresponding to a
1.75 nm etch depth per step, followed by acquisition of high-resolution spectra of V 2p,
Ni 2p, and O 1s peaks using a pass energy of 50 eV and a step size of 0.2 eV. The layer
compositions were determined from the measured area under the curves after Shirley
background subtraction and using the sensitivity factors within the PHI MultiPak
software package.

**III. RESULTS AND DISCUSSION**

Initial experiments focus on determining the required power to the deposition
sources and the suitable substrate temperature to achieve a stoichiometric composition
and to maximize atomic ordering, respectively. Figure 1(a) shows the measured
resistivity \( \rho \) as a function of V concentration from a series of 33.5 nm-thick VNi\(_2\) layers
deposited at \( T_s = 700 \) ℃ with a varying power of 45-60 W to the Ni deposition source
to obtain a range of compositions near the desired V:Ni = 1:2 ratio. The composition in
the \( x \)-axis is obtained from XPS depth profiles. An example is shown as supplementary
Figure S1. The depth profiles indicate a constant composition throughout the thickness
of the layer and a negligible oxygen impurity concentration below the surface
contamination which is attributed to water adsorption and/or surface oxidation during
transfer in air from the deposition to the XPS analysis chamber. The plotted resistivity
in Fig. 1(a) is a strong function of the composition, exhibiting pronounced minima of
54.4 and 40.2 µΩ cm at 293 and 77 K, respectively, at a composition of 34.3 at% V and 65.7 at% Ni. This measured composition is close to the expected 33.3:66.7 ratio for stoichiometric VNi$_2$, suggesting a resistivity minimum for the stoichiometric VNi$_2$ compound.

We attribute the composition dependence of the resistivity to the level of atomic ordering within the VNi$_2$ compound. The resistivity contribution from electron alloy scattering is described with Rossiter’s formula which relates the residual resistivity to the order parameter $S$ using $^{38}$

$$\rho(S) = \rho_r \frac{1-S^2}{1-AS^2}. \quad (1)$$

Here, $\rho(S)$ is the bulk residual resistivity (at zero temperature), $\rho_r$ is the resistivity of the completely random compound ($S = 0$) at $T = 0$, and $A$ is a parameter between 0 and 1 depending upon the position of the Fermi surface in relation to the superlattice Brillouin-zone boundaries. $^{39}$ The order parameter $^{40}$

$$S = \frac{r_\alpha - x_A}{y_\beta} = \frac{r_\beta - x_B}{y_\alpha} \quad (2)$$

depends on the fractions $r_\alpha$ and $r_\beta$ of $\alpha$ and $\beta$ sites being occupied by the correct (V and Ni) atoms, $x_A$ and $x_B$ are the atomic fractions of V and Ni within the layer and $y_\alpha = 0.333$ and $y_\beta = 0.667$ denote the fraction of $\alpha$ and $\beta$ sites. We note that $r_\alpha = x_A$ for a completely random alloy, resulting in $S = 0$. In contrast, if all Ni atoms occupy $\alpha$ sites, then $r_\alpha = x_A/y_\alpha$ for $x_A < y_\alpha$ and $r_\alpha = 1$ for $x_A > y_\alpha$, yielding a maximum $S = 1$ only at the stoichiometric $x_A = y_\alpha$. We expect some disorder even at a stoichiometric composition and therefore define $S_{\text{max}} < 1$ as the order parameter at $x_A = y_\alpha$, while $S$ decreases for deviations above and below the stoichiometric composition. Correspondingly, a linear approximation for $r_\alpha$ yields:

$$r_\alpha = x_A (1 - S_{\text{max}}) + S_{\text{max}} \cdot \min \left( \frac{x_A}{y_\alpha}, 1 \right) \quad (3)$$

and plugging $r_\alpha$ back into Eq. (2) provides an expression for the composition dependence of $S$:

$$S = \frac{S_{\text{max}}}{y_\beta} \cdot \left[ \min \left( \frac{x_A}{y_\alpha}, 1 \right) - x_A \right]. \quad (4)$$

The only unknown parameter in Eq. (4) is the order parameter $S_{\text{max}}$ at stoichiometric
composition. Plugging Eq. (4) into Eq. (1) yields the blue curve in Fig. 1(a) through the 77 K datapoints and values for the three fitting parameters $S_{\text{max}} = 0.95$, $\rho_r = 106 \mu\Omega \text{cm}$, and $A = 0.80$. The latter value is relatively large in comparison to the common range for $A = 0.3-0.5$, the value for $\rho_r$ suggests a resistivity of 106 $\mu\Omega \text{cm}$ for a VNi$_2$ alloy with random lattice occupation, and $S_{\text{max}} = 0.95$ corresponds to $r_x = 0.97$ for $x_A = y_A$, suggesting that approximately 3% of V atoms occupy Ni-sites at a stoichiometric composition. We note that these fitting parameters are correlated, resulting in considerable uncertainty in their values as, for example, a smaller $A$ and a larger $\rho_r$ yield a curve that matches the measured data nearly as well. Also, the fitting procedure neglects the resistivity contribution from electron-phonon scattering at 77 K, which is comparable in magnitude to the experimental uncertainty and is estimated to be 2-3 $\mu\Omega \text{cm}$ assuming that, as known for Ni, electron phonon scattering in perfectly ordered VNi$_2$ at 77 K is only 15% of the value at 293 K. The red datapoints in Fig. 1(a) from the 293 K measurements are approximately 15 $\mu\Omega \text{cm}$ above the 77 K values for all compositions, indicating additive resistivity contributions from electron scattering at phonons and lattice defects. That is, Matthiessen’s rule applies, indicating that the compositional variation has a negligible effect on the electronic structure and/or crystalline phase. This is also consistent with our XRD analyses (see supplementary Figure S2), indicating a single VNi$_2$ phase for all layers. We note that the temperature coefficient of resistivity is positive and nearly identical for all samples within the investigated composition range. This indicates that all layers exhibit metallic conduction with negligible carrier localization within the measured temperature range $T \geq 77$ K. Correspondingly, coulomb interactions and quantum (interference) effects are negligible for our investigation as the characteristic temperature for carrier localization is well below the investigated temperature range. The temperature effect is attributed purely to electron-phonon scattering and the composition/disorder effect is purely attributed to scattering at potential perturbations.

Figure 1(b) shows a corresponding plot of the measured $\rho$ as a function of $T_s = 20-850$ °C for a constant composition of 34.3 at% V. The resistivity exhibits a minimum.
for the layer deposited at 700 ℃ but increases at both lower and higher growth temperatures, which is attributed to kinetic barriers for atomic ordering and a thermodynamic driving force for disorder, respectively. The lower atomic ordering also results in a slightly reduced crystalline quality, as quantified by XRD rocking curves shown as supplementary Figure S3, indicating a 2-9% higher full width at half maximum (FWHM) of 1.32° and 1.41° for $T_s = 400$ and 850 ℃, respectively, than the 1.29° for the layer with the lowest resistivity grown at $T_s = 700$ ℃. Reducing $T_s$ further to room temperature dramatically degrades the crystallinity, so that no VNi$_2$ XRD peak can be detected (Figure S3), resulting in a high resistivity of 250 μΩ cm that is primarily attributed to the limited crystallinity. This value is 2.4 times larger than the fitted value of $\rho_r = 106$ μΩ cm for the alloy with complete atomic disorder ($S = 0$) but good crystallinity. In contrast, the measured 85.5 and 65.5 μΩ cm for $T_s = 400$ and 850 ℃ are well below $\rho_r$ and can therefore be primarily attributed to a reduced $S < 1$. As mentioned above, the reduction in ordering at low temperature ($T_s = 400$ ℃) is attributed to kinetic barriers. At higher temperatures ($T_s = 850$ ℃), the entropy from atomic disorder represents a thermodynamic driving force that causes the atomic long-range order parameter $S$ to decrease exponentially as the temperature is increased from approximately 50% to 100% of the critical transition temperature $T_C$ for complete randomization.40,48 We estimate the transition temperature for VNi$_2$ to be 1872 K, based on $T_C = -4W_1/k_B$ where $k_B$ is the Boltzmann constant and $W_1$ is the formation energy of a single A-B bond (with respect to the average of A-A and B-B bonds),40 estimated to be 40 meV based on the reported VNi$_2$ formation energy of 0.242 eV per atom.32 Thus, we expect entropy-driven disorder to develop above 50% of $T_C$, which corresponds to 936 K (663 ℃). This is in good agreement with our experimental observation of an increasing $\rho$ with $T_s > 700$ ℃. We note that 850 ℃ is well below the melting point of both V49 and Ni50 so evaporation is not considered in our work.

Figure 2 shows representative XRD and XRR results from a stoichiometric 33.5-nm-thick VNi$_2$ layer deposited on MgO(001) at $T_s = 700$ ℃. The $\theta$-2$\theta$ pattern in Fig. 2(a) exhibits a strong doublet feature at 42.92° and 43.04° from MgO 002 substrate
reflections of the Cu Kα₁ and Kα₂ x-rays. The peak at $2\theta = 50.59^\circ$ is ascribed to a combination of the 020 and 103 reflections of VNi₂. It is the only layer peak that can be detected over the entire measured $2\theta = 10$-80° range, implying the absence of detectable misoriented grains or secondary phases. Thus, the pattern suggests a single out-of-plane crystalline orientation which, however, can be VNi₂ 020 and/or 103. More specifically, the reported interplanar spacings range from 0.1774-0.1788 nm for 020 planes and from 0.1786-0.1818 nm for 103 planes, such that $d_{020}$ and $d_{103}$ vary by only 0.1-1.7%, corresponding to an expected $2\theta$ difference of 0.12-0.90°.²¹,³³,³⁴ This $2\theta$ range has a comparable magnitude as the measured 0.7° full width at half maximum (FWHM) of the peak in the measured $\theta$-2$\theta$ pattern. Thus, this peak cannot resolve the difference between VNi₂ 020 and 103. In fact, the peak width corresponds to an out-of-plane x-ray coherence length⁵¹ of 14 nm which is considerably smaller than the layer thickness of 33.5 nm, suggesting atomic disorder that corresponds to a domain size along the growth direction of approximately 14 nm. Similarly, the $\omega$ rocking curve of the VNi₂ 020/103 reflection shown in the inset of Fig. 2(a) has a FWHM of 1.3°. This may be attributed to a 1.3° mosaicity (crystalline tilt variability) but also corresponds to an in-plane coherence length of 8.0 nm, suggesting in-plane atomic disorder consistent with 8.0 nm wide VNi₂(020) and VNi₂(103) domains. Nevertheless, despite these complications due to the structural multiplicity which is further discussed below, the XRD peak demonstrates the formation of the ordered VNi₂ phase. Secondly, the peak position provides a measured value for the interplanar spacing of 0.1804 nm. This is 1.3 and 0.1 % larger than the reported $d_{020}$ and $d_{103}$,²¹,³³ indicating in-plane compressive stress which is attributed to differential thermal contraction during cooling from the $T_s = 700$ °C growth temperature. Thirdly, the rocking curve indicates good out-of-plane crystalline alignment and suggests epitaxial growth, comparable to previously reported rocking curves for other intermetallic compounds deposited on MgO(001) including CuAl²⁴ and CuTi²⁶.

The epitaxy is confirmed by XRD azimuthal $\varphi$-scans, as shown in Fig. 2(b). The plot shows at the bottom the asymmetric MgO 113 reflections obtained by tilting the
sample by $\chi = 25.23^\circ$ and fixing $2\theta = 74.74^\circ$. This yields four peaks at $\phi = 45, 135, 225, 315^\circ$, as expected from the four-fold symmetric single-crystal MgO(001) substrate. The top pattern is acquired with $\chi = 54.8^\circ$ and $2\theta = 43.8^\circ$ to detect VNi$_2$ 013 and/or 110 reflections. The VNi$_2$ (013) and (110) planes have nearly identical interplanar spacings and are also expected at the nearly same $54.8^\circ$ tilt for VNi$_2$ [010] or [301] out-of-plane directions, respectively. The plot shows four-fold symmetric peaks at the same $\phi$ values as for the MgO 113 peaks, indicating a single in-plane orientation of the VNi$_2$(010)/(103) layer. The peak width in $\phi$ is $<1.5^\circ$ for all four peaks, indicating a strong in-plane crystalline alignment. The combined results in Figs. 1(a) and (b) demonstrate epitaxial growth of VNi$_2$ on MgO(001), where either VNi$_2$(010) $\parallel$ MgO(001) and VNi$_2$[100] $\parallel$ MgO[110], or VNi$_2$(103) $\parallel$ MgO(001) and VNi$_2$[010] $\parallel$ MgO[100], as also illustrated in Fig. 3 and discussed below. Similar XRD results were obtained for all samples in this study of VNi$_2$ layers, confirming their epitaxy.

Figure 2(c) shows XRR results from the same layer. The measured intensity is plotted as solid red line in a logarithmic scale as a function of the scattering angle $2\theta = 0.1 – 3.0^\circ$. The plot includes the result from data fitting as dotted purple line, which is offset by a factor of 5 for clarity purposes and describes the measured data well. The fitting procedure yields a thickness $d = 33.5 \pm 0.7$ nm which is consistent with the expected 35 nm from deposition rate calibrations. It also provides values for a surface oxide thickness of 2.8 nm and a root-mean-square (RMS) surface roughness of 0.9 nm. Similar XRR analyses were conducted for a series of stoichiometric VNi$_2$ layers deposited at $T_s = 700$ °C, as shown as supplementary Figure S4. They provide values of $d = 10.5 \pm 0.3, 21.0 \pm 0.5, 33.5 \pm 0.7, 77.2 \pm 1.5$ nm for VNi$_2$ layers which are covered by a 0.4, 1.3, 1.9, 2.3 nm thick surface oxide with a 0.3, 0.4, 0.9 and 0.1 nm roughness. That is, all layers have surface oxides that are thinner than 3 nm, consistent with XPS depth profile measurements, and have smooth surfaces with a roughness below 1 nm.

Figure 3 illustrates the epitaxy of VNi$_2$ on MgO(001). The schematic in Fig. 3(a) shows the conventional unit cell of VNi$_2$ which adopts an orthorhombic crystal
structure with \( a = 2.52 \, \text{Å}, \, b = 3.57 \, \text{Å}, \) and \( c = 7.59 \, \text{Å} \). This system exhibits almost perfect relationships between lattice constants with \( b \cong \sqrt{2}a \) and \( c \cong 3a \), such that each atom is 12-fold coordinated with a nearest neighbor distance of 2.52 Å. Thus, when disregarding atom types, the structure forms a slightly distorted face-centered cubic (fcc) structure where the \([301]_{\text{VNi}_2}, [010]_{\text{VNi}_2}, \) and \([301]_{\text{VNi}_2}\) directions of \( \text{VNi}_2 \) are parallel to the \([100]_{\text{fcc}}, [010]_{\text{fcc}}, \) and \([001]_{\text{fcc}}\) lattice vectors of the fcc parent structure. Figs. 3(b) and (c) illustrate how these particular relations enable two epitaxial \( \text{VNi}_2 \) layer orientations on \( \text{MgO}(001) \) with exactly the same atomic positions but a different ordering of V and Ni atoms. More specifically, Fig. 3(b) shows the case for a \( \text{VNi}_2(010) \) layer. The cubes drawn with black lines indicate the conventional unit cell of the fcc structure, which exhibits a cube-on-cube epitaxy with the \( \text{MgO}(001) \) substrate such that \([010]_{\text{fcc}}\) and therefore also \([010]_{\text{VNi}_2}\) point in the growth direction. The V and Ni atoms (orange and gray) occupy positions above the oxygen atoms (red) of the MgO substrate. Similarly, the atoms of the \( \text{VNi}_2(103) \) layer shown in Fig. 3(c) also sit on top of the oxygen atoms of the substrate, yielding again a cube-on-cube epitaxy of the parent fcc structure on \( \text{MgO}(001) \). In this case, the out-of-plane growth direction corresponds to the \([100]_{\text{fcc}}\) and, in turn, the \([301]_{\text{VNi}_2}\) crystalline direction. In summary, both \( \text{VNi}_2(010) \) and \( \text{VNi}_2(103) \) form an epitaxial layer on \( \text{MgO}(001) \) with a cube-on-cube epitaxy of the parent fcc structure. However, the cubes of the fcc structure which are drawn with black lines in Fig. 3(b) and (c) do not represent repeating unit cells if considering the atom type (V or Ni) such that the atomic positions in the two figures are identical but not the color which represents the atom type. Correspondingly, the structure of our \( \text{VNi}_2/\text{MgO}(001) \) can be described by a single crystal layer consisting of both \( \text{VNi}_2(010) \) and \( \text{VNi}_2(103) \) domains or alternatively as an epitaxial fcc V-Ni(001) alloy which exhibits regions that exhibit atomic ordering to form locally a \( \text{VNi}_2 \) compound. We note that the XRD signature for each of these descriptions is a single peak that indicates a \( d \)-spacing corresponding to the lattice constant of the fcc parent structure, as discussed above. Similar structural ambiguity has previously been reported for pseudo-hexagonal \( \text{AB}_2 \) layers where the ordered phase forms a MoPt\(_2\)-type crystal structure.\(^{33,52}\)
epitaxial system illustrated in Fig. 3 exhibits a relatively large 15% lattice mismatch. Nevertheless, MgO(001) is the only investigated substrate (see also previous section) that leads to epitaxial VNi$_2$ growth. We attribute the epitaxy to the preferential cube-on-cube epitaxy system which has previously been applied to the growth of epitaxial fcc metals including Cu$^{53,54}$ and Ni$^{42}$ on MgO(001), despite similarly large mismatches of 14% and 16 %, respectively.

Figure 4 shows the measured resistivity $\rho$ as a function of thickness $d = 10.5$-138 nm of epitaxial VNi$_2$(010)/(103) layers. The plot includes $\rho$ measured in situ at room temperature (293 K) as red circles, in liquid N$_2$ at 77 K as blue squares, and ex situ after air exposure at 293 K as grey open circles. The in situ $\rho$ increases with decreasing thickness from $50.6 \ \mu\Omega \ \text{cm}$ at $d = 138$ nm to $103.8 \ \mu\Omega \ \text{cm}$ at $d = 10.5$ nm. The corresponding increase at 77 K is from $36.4$ to $87.4 \ \mu\Omega \ \text{cm}$. We attribute these increases to electron scattering at the layer surfaces. The resistivity at 77 K is smaller than at room temperature. This is due to reduced electron-phonon scattering at cryogenic temperatures and is, to first order, independent of other scattering mechanisms such that the red and blue data points in Fig. 4 are separated by an approximately constant $\Delta \rho = 12.9$-19.6 $\mu\Omega \ \text{cm}$, consistent with the $15 \ \mu\Omega \ \text{cm}$ from Fig. 1(a). The $\Delta \rho$ represents the difference in the resistivity contribution from electron-phonon scattering at 293 and 77 K. This value is comparable to the previously reported first-principle prediction of $13.9 \ \mu\Omega \ \text{cm}$ for the VNi$_2$ room temperature bulk resistivity along the [100] direction, but smaller than the predictions of $25$ and $70 \ \mu\Omega \ \text{cm}$ along [010] and [001].$^{21}$ The plotted datapoints for the room temperature resistivity after air exposure are shifted by 2 nm to the left to account for the reduction in the effective conductive thickness during air exposure, as quantified from the measured 0.4-2.3 nm surface oxide by assuming stoichiometric VNi$_2$ oxide with an estimated density of 4.5 g/cm$^3$. These ex situ values are 1.8-3.1 % above the in situ resistivity, which may be attributed to an increase in diffuse electron surface scattering due to localized surface states$^9$ or charge transfer at oxygen-exposed surfaces$^7$ similar to what has previously been reported for Nb(001),$^{55}$ Cu(001),$^{56,57}$ Co(0001),$^8$ Ni(001),$^{42,58}$ and Mo.$^59$ However,
the relative resistivity increase during air exposure of our VNi$_2$ layers is quite small, which we attribute to relatively large resistivity contributions from electron scattering at phonons and atomic disorder i.e. domain boundaries. We note that we have deposited another VNi$_2$ layer with a nominal thickness of 6.7 nm. However, it is not included in Fig. 4 because it shows an infinitely high resistance caused by a discontinuous microstructure i.e. incomplete substrate coverage, similar to what has previously been reported for Ir(001) layers with $d < 5$ nm.\textsuperscript{18}

The curves in Fig. 4 are obtained by data fitting using the FS model.\textsuperscript{12,13} For this purpose, we assume surface scattering to be completely diffuse ($p = 0$) while the bulk electron mean free path $\lambda$ and the bulk resistivity $\rho_o$ are free fitting parameters. Setting the specularity parameter $p$ to 0 is used because the parameters $p$ and $\lambda$ in the FS model are strongly correlated and typically cannot be independently determined from measured $\rho$ vs $d$ data.\textsuperscript{55,60,61} This analysis approach with $p = 0$ has previously been employed to quantify the resistivity scaling for various metals like Ru,\textsuperscript{16,62} Co,\textsuperscript{8} W,\textsuperscript{63} and Ni,\textsuperscript{42} and yields an effective $\lambda_{\text{eff}}$ that represents a lower bound of possible $\lambda$ values. Data fitting of the measured room temperature resistivity yields the red curve and $\rho_o = 46 \pm 2$ $\mu\Omega$ cm and $\lambda_{\text{eff}} = 30 \pm 5$ nm. This bulk resistivity is approximately three times larger than the previous theoretical prediction of 13.9 $\mu\Omega$ cm along [100] direction.\textsuperscript{21} We attribute this disagreement to a higher measured resistivity caused by electron scattering at domain boundaries (i.e. atomic disorder), as illustrated in Fig. 3, but also note that the predicted resistivity along perpendicular [010] and [001] is 1.8 and 5 times higher than along [100], respectively.\textsuperscript{21} Applying the same analysis to the \textit{ex situ} data results in a slightly larger $\lambda_{\text{eff}} = 32$ nm which is consistent with the measured resistivity increase during air exposure. However, this value is within the error range of the \textit{in situ} measured $\lambda_{\text{eff}}$, indicating that surface oxidation has a negligible effect on electron scattering in our layers, which may be attributed to the large competing contribution from electron scattering at domain boundaries.

Analysis of the 77 K data yields $\rho_o = 32 \pm 2$ $\mu\Omega$ cm and $\lambda = 50 \pm 6$ nm. The cryogenic bulk resistivity is only 31 % below the room temperature value, confirming
that a temperature-independent electron scattering mechanism (domain walls / atomic disorder) dominates the overall resistivity. We determine the product $\rho_o \lambda = (160 \pm 10) \times 10^{-16} \, \Omega m^2$ at 77 K and $(138 \pm 5) \times 10^{-16} \, \Omega m^2$ at 293 K. This product is used as a benchmark to determine promising conductors for narrow lines. It is quite large, approximately an order-of-magnitude higher than for most competing metals, indicating that VNi$_2$ exhibits a large resistivity size effect. We note that the $\rho_o \lambda$ product is, to first order, independent of the magnitude of bulk scattering since additional scattering causes an increase in $\rho_o$ but a corresponding decrease in $\lambda$, keeping the $\rho_o \lambda$ product constant. Therefore, $\rho_o \lambda$ is expected to be temperature-independent, consistent with the similar values measured at 77 and 293 K. In addition, the $\rho_o \lambda$ is expected to be unaffected by defect scattering at antisite defects and domain boundaries. Correspondingly, a measured $\rho_o \lambda$ should represents the intrinsic value for VNi$_2$, independent of the level of atomic ordering. Based on this argument, our large measured $\rho_o \lambda$ would imply that VNi$_2$ is not promising as conductor for narrow interconnects. However, we expect that the level of atomic ordering increases with layer thickness since columnar growth results in an increasing domain size with increasing thickness. As a result, the measured resistivity size effect presented in Fig. 4 is likely exacerbated by electron scattering at atomic disorder and domain walls, which become more pronounced for small $d$. That is, we expect the resistivity scaling for intrinsic VNi$_2$ to be considerably smaller than the measured $\rho_o \lambda$ suggests. Thus, our negative conclusion about the promise of VNi$_2$ as interconnect material is a consequence of insufficient atomic ordering, while a different processing scheme that yields ordered and directional VNi$_2$ may be able to confirm the promising theoretical predictions for this compound.

**IV. CONCLUSIONS**

Sputter deposition of orthorhombic VNi$_2$ on MgO(001) results in epitaxial layers which exhibit domains with a VNi$_2$(010) or VNi$_2$(103) orientation that are separated by anti-phase boundaries but share the same fcc parent structure that forms a cube-on-cube epitaxy with the substrate. Measurements of the resistivity vs
composition indicate a minimum for stoichiometric (V:Ni = 1:2) layers, while deviations from this composition result in a decrease in the order parameter which leads to electron scattering at antisite defects and domain boundaries and a correspondingly higher resistivity. The highest atomic ordering is achieved at a growth temperature of 700 °C, while lower and higher temperatures cause increased atomic disorder attributed to kinetic barriers for ordering and an entropic driving force for disorder, respectively. The measured $\rho$ increases with decreasing layer thickness $d$. Data fitting with the Fuchs-Sondheimer model yields a room temperature bulk resistivity $\rho_o = 46 \pm 2 \, \mu\Omega \, \text{cm}$ and $\rho_o \lambda = (138 \pm 5) \times 10^{-16} \, \Omega \, \text{m}^2$, while the corresponding values at 77 K are $\rho_o = 32 \pm 2 \, \mu\Omega \, \text{cm}$ and $\rho_o \lambda = (160 \pm 10) \times 10^{-16} \, \Omega \, \text{m}^2$. The measured resistivity is considerably higher than what was previously predicted. This is attributed to electron scattering at domain boundaries / atomic disorder. In addition, the resistivity scaling as quantified by the $\rho_o \lambda$ product is higher than for many competing metals, suggesting that VNi$_2$ is not promising as conductor for narrow interconnects. However, the high experimental $\rho_o \lambda$ may be attributed to a thickness-dependent atomic ordering. In that case, VNi$_2$ is a promising interconnect material if a synthesis scheme can be developed that results in strong atomic order, a negligible domain boundary density, and a [100] crystalline orientation along the transport direction.

**Supplementary Material**

Supplementary Material to this paper includes additional figures presenting x-ray photoelectron spectroscopy, x-ray diffraction, and x-ray reflectivity data.

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Figure 1. Electrical resistivity $\rho$ measured *in situ* (red) at room temperature and in liquid N\(_2\) (blue) versus (a) the concentration of V and (b) the substrate temperature $T_s$ during deposition of VNi\(_2\) layers with thickness $d = 33.5$ nm. The blue curve in (a) is the result from data fitting using Eq. (1).
Figure 2. Representative (a) XRD $\theta$-2$\theta$ scan with $\omega$ rocking curve of the VNi$_2$ 020/103 reflection in the inset, (b) azimuthal $\varphi$-scan of VNi$_2$ 013/110 and MgO 113 reflections, and (c) XRR scan including the result from curve fitting, from a 33.5-nm-thick VNi$_2$/MgO(001) layer deposited at $T_s = 700$ °C.

Figure 3. Schematics of (a) the orthorhombic conventional VNi$_2$ unit cell, (b) epitaxial VNi$_2$(010) and (c) epitaxial VNi$_2$(103) deposited on MgO(001).
Figure 4. Resistivity $\rho$ vs thickness $d$ of epitaxial VNi$_2$(010)/(103) layers, measured \textit{in situ} in vacuum at 293 K, in liquid N$_2$ at 77 K, and \textit{ex situ} in air at 293 K.

Figure S1. XPS depth profile from a 33.5-nm-thick VNi$_2$ layer on MgO(001).

Figure S2. XRD patterns of samples with different compositions, showing no detectable secondary phases.
| Figure S3. XRD patterns and $\omega$ rocking curve of the VNi$_2$ 020/103 reflection of samples deposited at different temperatures. |
| Figure S4. Measured (solid) and fitted (dotted) XRR curves of a series of VNi$_2$ thin films with different thickness. |