The structural and magnetic phase transition in CrN has recently attracted considerable interest, due to a possible band gap \(^1\,^2\) in CrN and the related promise as a spintronic material. \(^3\,^4\) Electronic transport studies report controversial results for CrN, including the following: (1) values for the resistivity \(\rho\) at room-temperature range over more than two orders of magnitudes, from \(1.7 \times 10^{-3}\) to \(3.5 \times 10^{-1}\) \(\Omega\)cm. \(^5\,^6\,^7\,^10\) even when considering only the most reliable data for single-crystal CrN layers; (2) the temperature dependence of \(\rho\) shows metallic behavior with \(d\rho/dT > 0\) in some studies. \(^6\,^7\,^11\) but an increase in \(\rho\) with decreasing temperature in other reports, \(^3\,^5\,^9\,^12\) which has been attributed to the presence of a band gap \(^5\) or carrier localization due to crystalline defects \(^13\) or N vacancies; \(^14\) (3) some studies report a discontinuity in \(\rho(T)\) at 260–280 K. \(^3\,^6\,^7\,^14\) which is associated with a magnetic and structural phase transition from a paramagnetic NaCl structure at room temperature to a low-temperature antiferromagnetic orthorhombic \(P_{\text{mna}}\) phase \(^1\,^7\,^15\) with a 0.56%-0.59% higher density, \(^11\) and a 25% lower bulk modulus. \(^16\) while other reports show no evidence for a phase transition in the \(\rho(T)\) curves. \(^5\,^7\,^9\) Electronic structure calculations suggest that magnetic stress relief couples magnetic ordering with the structural phase transition, \(^17\) and that CrN exhibits a band gap if the Hubbard Coulomb interaction term is sufficiently large. \(^2\)

In this report we demonstrate that CrN layers grown under identical conditions but on different substrates can exhibit transport properties that vary by several orders of magnitudes, providing insight into the reasons for the reported controversial results as well as into the fundamental electronic transport properties. In particular, CrN layers were deposited by ultra-high-vacuum reactive magnetron sputtering onto MgO(001), MgO(111), and quartz substrates following the procedure described in Refs. 10 and 18. This results in epitaxial CrN(001) and CrN(111) as well as polycrystalline CrN layers, respectively. The combination of temperature-dependent x-ray diffraction (XRD) and electronic transport measurements show that: (1) increasing crystalline quality and decreasing N-vacancy concentration reduce the conductivity in single-crystal CrN; (2) the cubic high-temperature phase exhibits (insulating) hopping conduction while the orthorhombic low-temperature phase is metallic with a positive or negative \(d\rho/dT\) depending on disorder localization; (3) polycrystalline layers exhibit a phase transition at 270–287 K while single-crystal layers remain in the cubic high-temperature phase down to 10 K.

Both single- and polycrystalline CrN layers are grown by reactive sputtering on MgO and quartz substrates, respectively. Temperature-dependent x-ray diffraction indicates a phase transition near 280 K to a low-temperature orthorhombic phase for polycrystalline CrN, while epitaxial constraints cause single-crystal CrN(001) and CrN(111) to remain in the cubic high-temperature phase. Electronic transport measurements indicate variable-range-hopping for the cubic phase below \(\sim 120\) K, a discontinuity at the phase transition for the polycrystalline layers, strongly and weakly disordered metallic conduction for the orthorhombic phase if deposited at 600 and 800 °C, respectively, and a disorder-induced metal-insulator transition in the cubic phase.
it cannot be made with any certainty, since the error bars of
the individual data points allow equally well the fitting with a
straight line for the whole temperature range, as shown in the
plot.

Figure 1(b) also shows the corresponding values determined
using the CrN 002 reflection from a 140-nm-thick polycrys-
talline CrN layer grown on a quartz substrate at 800 °C, where
both CrN 111 and 002 are present in the ω-2θ spectra with
2θ = 20°–50° (not shown). The error bars for this layer
are larger, due to the broader peak width associated with
the smaller layer thickness and the finite grain size. The
line through the data is obtained using Boltzmann sigmoidal
fitting with an additional linear term corresponding to the
α from the epitaxial layer. The data clearly show a 0.14%
increase of lattice constant at 270–284 K, indicating a phase
transition for the polycrystalline CrN layer. The 0.14%
increase is within previously reported values of 0.08%7
and 0.24%, 11 where the relatively large difference between
these studies is likely due to impurities, particularly for
bulk samples, and substrate-induced stress for the thin-film
studies.

The phase transition in the polycrystalline CrN layers is
even more evident from the CrN 111 peak. The distortion of
the cubic to the orthorhombic phase causes a 1.2% increase
and a 1.2% decrease of the two-body diagonals in the original
cubic unit cell, corresponding to the 011 and 201 lattice
spacings in the new orthorhombic structure.16 Figure 1(c)
shows exemplary x-ray diffraction ω-2θ scans, including the
corresponding Lorentzian fitting, from a polycrystalline CrN
layer. The scans at 293 and 251 K exhibit a cubic CrN 111 and
an orthorhombic CrN 201 peak at 2θ = 37.57° and 37.98°,
respectively, while 284 K leads to a spectrum containing both
peaks, indicating that the phase transition occurs near this
temperature. The 011 peak could not be detected for any
of our samples, indicating that the structural relaxation into
the low-temperature orthorhombic phase preferentially occurs
with the primary contraction along the growth direction, which
we attribute to the lateral fixation by the substrate, which
suppresses considerable expansion or contraction in the plane
parallel to the substrate surface. The phase transition for the
polycrystalline layer is further illustrated in Fig. 1(d), which
is a plot of the 111 and 201 peak intensities versus T, obtained
by fitting a series of spectra as those shown in Fig. 1(c).
The spectra up to 273 K show only the orthorhombic 201 peak,
followed by a gradual transition where the 201 intensity
decreases and the 111 intensity increases, until 287 K, where
the structure is purely cubic. Thus, the phase transition occurs
at 273–287 K, which is consistent with the transition range of
270–284 K shown in Fig. 1(b).

Figure 2 is a semilog plot of the conductivity σ from six
representative CrN layers measured between 10 K and room
temperature using a Cryomagnetics Inc. 4He cryostat system
and a linear four-point probe geometry with sputter-deposited
Cu contacts. The 140-nm-thick CrN layers are grown at two
different temperatures T_s = 600 and 800 °C, and on three
different substrates, MgO(001), MgO(111), and fused quartz
glass, resulting in single-crystal CrN(001), CrN(111), and
polycrystalline CrN, respectively.

FIG. 2. (Color online) Conductivity σ versus T for six 140-nm-
thick CrN layers, deposited on three different substrates yielding
single-crystal CrN(001) and CrN(111) and polycrystalline CrN. Solid
and open symbols represent growth temperatures T_s = 600 and 800
°C, respectively. The lines are obtained from curve fitting. The inset
shows the data from the polycrystalline layers in a linear plot, to
highlight the discontinuity indicated by arrows.
All single-crystal CrN layers show a monotonous increase in $\sigma$ with increasing $T$ over the complete measured temperature range $T = 10–295$ K. The conductivity at room temperature is 700–3000 times larger than at 10 K, indicating that these CrN samples show insulating behavior. The data are fitted using a Mott variable-range hopping (VRH) conduction mechanism with $\sigma \propto T^{-1/4}$, as indicated by the lines through the single-crystal data in Fig. 2. Mott VRH describes well the temperature dependence of $\sigma$ for approximately 50–120 K, while there is some deviation at low ($T < 25$ K) and high ($T > 120$ K) temperatures, which are attributed to Efros-Shklovskii VRH and mobility edge conduction as discussed in detail for CrN(001) in Ref. 10. The absolute values for the conductivity strongly depend on both growth temperature and layer orientation. For example, $\sigma_{10K}$ decreases from 0.031 and 0.038 $\Omega^{-1}$ cm$^{-1}$ for CrN(001) to 0.018 and 0.0014 $\Omega^{-1}$ cm$^{-1}$ for CrN(111) grown at $T_s = 600$ and 800 °C, respectively. This is attributed to an expected lower activation barrier for N$_2$ dissociation and incorporation on polar CrN(111) surfaces than on nonpolar CrN(001), due to a higher planar density of N atoms, 1.32 versus 1.14 $\times$ 10$^{15}$ atoms/cm$^2$, respectively. This results in a lower N vacancy concentration and therefore a lower hopping conduction for CrN(111), particularly at high $T_s$.

The polycrystalline CrN layers are one-to-three orders of magnitudes more conductive than epitaxial CrN. This higher conductivity particularly at low temperatures suggests metallic transport for the polycrystalline layers. This is consistent with a much weaker temperature dependence, with $\sigma(T)$ varying only by a factor of two within 10–290 K. The temperature dependence is highlighted in the linear-scale plot in the inset of Fig. 2, which also reveals a drop in $\sigma(T)$ between 270 and 287 K. This is a clear indication for a phase transition in our polycrystalline layers, confirming the XRD results. The change in $\sigma$ at the phase transition is 2% and 6% for $T_s = 600$ and 800 °C, respectively, which is smaller than previously reported changes of 10%, 20%, 7,28 30%, 11 or 120%, 5 and may be related to differences in defect density, preferred orientation, and/or stress level for the different studies. All reports agree that the low-temperature antiferromagnetic phase has a higher conductivity than the paramagnetic phase.

The solid lines through the data points for the polycrystalline CrN in Fig. 2 are obtained by fitting the conductivity of the antiferromagnetic phase for $T = 10–255$ K using

$$\sigma(T) = \frac{1}{\rho^*(T)} + C T^{1/2},$$

where $C T^{1/2}$ accounts for the Coulomb interaction at low temperature and $\rho^*(T)$ is the nominal temperature-dependent resistivity of a metal. The data for $T_s = 600$ °C are best described with a linear $\rho^*(T) = \rho_o + B T^2$, where $d\rho/dT = A = -4.87 \times 10^{-5}$ K$^{-1}$ is negative. We attribute $d\rho/dT < 0$ to strong disorder, 29 as commonly observed for amorphous metals, and conclude that the antiferromagnetic phase is metallic, particularly because $d\ln(\sigma)/d\ln(T) \rightarrow 0$ as $T \rightarrow 0$, a criteria that has been previously used to discuss conduction in CrN. The data for $T_s = 800$ °C are better described with $\rho^*(T) = \rho_o + B T^2$, where the parabolic temperature dependence is due to Boltzmann transport associated with electron-electron scattering in a weakly disordered metallic system, similar to what has been reported for ZnO 31 and LaNiO$_3$. That is, the polycrystalline layers grown at $T_s = 600$ and 800 °C exhibit both metallic conduction but strong and weak disorder, respectively, which is attributed to the higher atom mobility and related crystalline quality at higher $T_s$. Above the phase transition, that is, at $T > 287$ K, the layer grown at $T_s = 600$ °C exhibits insulating properties, supporting the conclusion from the single-crystal data that the high-temperature paramagnetic phase is insulating. However, the polycrystalline layer with $T_s = 800$ °C exhibits metallic behavior, comparable to some previous studies that found $d\rho/dT > 0$ above the Néel temperature. 7,11 We believe that this is likely due to (1) an N vacancy concentration that is above the critical concentration for the Mott metal-insulator transition or (2) a sufficiently high defect concentration to cause delocalization, that is, an Anderson metal-insulator transition. 33 These two mechanisms may, in fact, be simultaneously effective. That is, the polycrystalline layer with $T_s = 600$ °C has strong disorder, which prevents the metal-insulator transition in the high-temperature phase, while its counterpart with $T_s = 800$ °C is weakly disordered which facilitates the transition.

In summary, the x-ray diffraction results clearly show that our polycrystalline samples grown on quartz glass at $T_s = 600–800$ °C exhibit the reported phase transition from a high-temperature cubic phase to a low-temperature orthorhombic phase at 280 ± 5 K, with the transition likely being facilitated by underdense grain boundaries that allow grain slip and, in turn, independent shear deformation for each grain. In contrast, epitaxial CrN(001) and CrN(111) layers grown under identical conditions but on MgO(001) and MgO(111) substrates, remain in the cubic phase over the entire measured temperature range. We attribute the absence of a phase transition to epitaxial constraints that suppress the shear deformation into the orthorhombic structure, as this would require an instantaneous macroscopic transition of the entire layer. This is in agreement 5 and disagreement 6 with previous reports on a phase transition in epitaxial CrN. The comparison in this study of polycrystalline and single-crystal CrN deposited under identical conditions suggests that the substrate and associated grain boundaries may more strongly affect the presence or absence of a phase transition than growth conditions or layer orientation. The XRD results are supported by $T$-dependent transport data, showing a discontinuity in $\sigma(T)$ between 270 and 287 K for polycrystalline CrN but a continuous curve for epitaxial layers. In addition, transport in cubic paramagnetic CrN is well explained by variable range hopping, while orthorhombic antiferromagnetic CrN exhibits strongly and weakly disordered metallic properties for $T_s = 600$ and 800 °C, respectively.

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20The value for aMgO (0.4213 nm is from the Inorganic Index to Powder Diffraction (Joint Committee on Powder Diffraction Standards, International Center for Powder Diffraction Data, Newtown Square, PA, 1998): MgO (Card No. 04-0829).
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