Epitaxial suppression of the metal-insulator transition in CrN

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Abstract

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 ~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.

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 spintronic material.[3,4] Electronic transport studies report controversial results for CrN, including (i) values for the resistivity ρ at room temperature range over more than two orders of magnitudes, from 1.7×10^{-3} to 3.5×10^{-1} Ωcm,[3, 5-10] even when only considering the most reliable data for single crystal CrN layers; (ii) the temperature dependence of ρ shows metallic behavior with $d\rho/dT > 0$ in some studies,[6,7,11] but an increase in ρ 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] (iii) 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_{nma} phase[11,15] 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 (i)

increasing crystalline quality and decreasing N-vacancy concentration reduce the conductivity in single crystal CrN; (ii) 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; (iii) 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.

Figure 1(a) shows a portion of three exemplary XRD ω-2θ spectra, obtained at 251, 284, and 293 K, from a 2.0-μm-thick epitaxial CrN/MgO(001) layer grown at T_s = 700 °C. The spectra were acquired with a PANanalytical X'Pert Pro diffractometer with a Cu $K\alpha$ source, a divergent beam geometry, an array detector, and a custom built cold stage. The only detected peaks in the measured 2θ range from 20 to 80° are the CrN 002 and the MgO 002 reflections, with the latter being split into a double peak feature at 2θ = 42.899° and 43.012° for the 293 K spectra, due to the $K\alpha$1 and $K\alpha$2 x-ray emission, respectively. The resulting MgO substrate lattice constant is 0.4213 nm at 293 K, and decreases to 0.4211 nm at 251 K, consistent with the reported room temperature lattice constant of 0.4212 nm [19] or 0.4213 nm, [20] and thermal expansion coefficient of 1.3×10^{-5} K^{-1}.[21] Similarly, the out-of-plane CrN lattice constant, which is determined using a weighted average source wavelength of 0.15418 nm, decreases due to thermal contraction from 0.4180 to 0.4178 nm for 293 and 251 K. This decrease of only 0.05% indicates the absence of a phase transition to the orthorhombic structure, which would yield a ~5× larger decrease due to the 0.24 % smaller lattice parameter.[11] In addition, the CrN peak intensity also decreases with decreasing temperature, which may be due to local strain fields associated with the suppressed phase transition. The change of the CrN lattice constant vs T is plotted in Fig. 1(b), as a ratio of the measured out-of-plane parameter c over the room temperature value c_0. The line through the data is obtained from a linear fit, providing a value for

the thermal expansion coefficient of $\alpha = 9.1\times10^{-6}$ K^{-1}, which is slightly larger than 7.16×10^{-6} K^{-1}, the value reported for CrN at elevated temperatures.[22] This larger measured α for the out-of-plane lattice constant is expected, because the differential thermal contraction between CrN layer and MgO substrate causes an increasing compressive strain with deceasing temperature. We also note that the data in Fig. 1(b) appears to show two distinct slopes: $\alpha = 9.4\times10^{-6}$ K^{-1} and $\alpha = 2.6\times10^{-6}$ K^{-1} below and above ~275 K, respectively. This suggests that the thermal expansion coefficient may change at the critical temperature for the phase transition ~275 K, even in the absence of an actual structural phase transition. Such a conclusion supports the recent report on a reduction in the bulk modulus,[16] however, 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.

Fig. 1(b) also shows the corresponding values determined using the CrN 002 reflection from a 140-nm-thick polycrystalline CrN layer grown on a quartz substrate at 800 °C, where both CrN 111 and 002 are present in the ω-2θ spectra with $2\theta = 20$-$50°$ (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 shows 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] Fig. 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 $2\theta = 37.57°$ 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 vs 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 semi-log plot of the conductivity σ from six representative CrN layers measured between 10 K and room temperature using a Cryomagnetics Inc ^{4}He 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.

All single crystal CrN layers show a monotonous increase in σ with increasing T over the complete measured temperature range T = 10-295 K. The conductivity at room temperature is 700-3000 larger than at 10 K, indicating that these CrN samples show insulating behavior. The data is fitted using a Mott variable-range hopping (VRH) conduction mechanism with $\sigma \propto T^{-1/4}$,[10,23] as indicated by the lines through the single crystal data in Fig. 2. Mott VRH describes well the temperature dependence of σ 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 (ES) VRH[24,25] and mobility edge conduction,[23, 26, 27] 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, σ_{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 non-polar CrN(001), due to a higher planar density of N-atoms, 1.32 vs 1.14×10^{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 1-3 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 2 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 to 287 K. This is a clear indication for a phase transition in our

polycrystalline layers, confirming the XRD results. The change in σ 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%,[3] 20%,[7,28] 30%,[11] or 120%,[6] 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 anti-ferromagnetic phase for $T = 10\text{-}255$ K using

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

where $CT^{\frac{1}{2}}$ accounts for the Coulomb interaction at low temperature[29] and $\rho^*(T)$ is the nominal temperature dependent resistivity of a metal. The data for $T_s = 600$ °C is best described with a linear $\rho^*(T) = \rho_o + AT$, 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 $d(\ln\sigma)/d(\ln T) \to 0$ as $T \to 0$,[30] a criteria which has been previously used to discuss conduction in CrN.[28] The data for $T_s = 800$ °C is better described with $\rho^*(T) = \rho_o + BT^2$, where the parabolic temperature dependence is due to Boltzmann transport associated with electron-electron scattering in a weakly disordered metallic system,[29] similar to what has been reported for ZnO[31] and LaNiO$_3$.[32] 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 (i) a N-vacancy concentration that is above the critical concentration for the Mott metal-insulator transition or (ii) 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[5,9] and disagreement[6,7] 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/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 to 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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Figure Captions

Figure 1: (a) Exemplary XRD ω-2θ scans from a 2-μm-thick CrN/MgO(001) sample at 251, 284, and 293 K. (b) Temperature dependence of the out-of-plane lattice constant c determined from the 002 peak position for single and polycrystalline CrN (c_o is the value at 293 K). (c) Corresponding ω-2θ scans from a 140-nm-thick polycrystalline CrN layer. (d) Intensity of CrN 111 and 201 peaks versus temperature.

Figure 2: Conductivity σ vs 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.

(a) Epitaxial CrN

MgO 002

CrN 002

Intensity (10^6 cps)

251 K
284 K
293 K

2θ (deg)

(b)

c/c_o

Epitaxial CrN

Polycrystalline CrN

T (K)

(c) Polycrystalline CrN

111

201

Intensity (10^3 cps)

251 K
284 K
293 K

2θ (deg)

(d) Polycrystalline CrN

Orthorhombic CrN 201

Cubic CrN 111

Intensity (arb. u.)

T (K)