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Solving the controversy of the metal-insulator phase transition in chromium nitride thin films

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Background incl. aims

CrN is a hard coating material that has applications in abrasion and wear-resistant cutting tools, bearings, and tribology applications due to its high hardness, high-temperature stability, and corrosion-resistant properties. Recently, CrN has also attracted significant interest due to its high thermoelectric power factor [1]. Much of debate in the literature is around CrN's unique and intriguing metal-insulator phase transition. While CrN bulk single-crystals exhibit the characteristic metal-insulator transition accompanied with structural (orthorhombic-to-rocksalt) and magnetic (antiferromagnetic-to-paramagnetic) transition at ~260 - 280 K, observation of such phase transition in thin-film CrN has been scarce, and the exact cause of the absence of the transition in several thin film studies is not well-understood [2].

Methods

STEM images and EDS maps were recorded with an image- and probe-corrected and monochromated Themis-Z 60-300 kV equipped with a high-brightness XFEG source and Super-X EDS detector system for ultra-high-count rates, operated at 300 kV. The spatial resolution in STEM mode was 0.7 Å. EDS maps used for atomic % quantification have well above 1 M counts, and k-factor analysis and absorption-corrected background subtraction were employed.

Results

Here, we demonstrate that the formation of a secondary metallic Cr2N phase during the growth inhibits the observation of metal-insulator phase transition in CrN thin films, see Figure 1. When the Cr-flux during deposition is reduced below a critical limit, an epitaxial and stoichiometric CrN thin film is obtained that reproducibly exhibits the phase transition. Annealing of the mixed-phase film inside reducing NH3 environment converts the Cr2N into CrN as revealed by HRSTEM imaging and EDS mapping, and a discontinuity in the electrical resistivity at ~277 K appears.

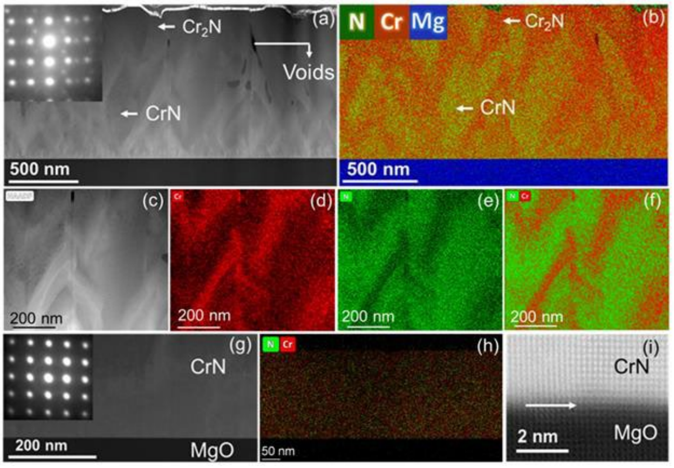
Conclusion

In summary, we show that formation of the secondary metallic Cr2N phase inside CrN during the thin film growth process inhibits the observation of its metal-insulator electronic phase transition. A high Cr-flux during the deposition process results in metallic Cr2N networks inside the CrN matrix. When the Cr-flux is reduced below the critical limit of the growth rate of 1 nm/min, a stoichiometric single-crystalline CrN thin film is obtained that reproducibly exhibits the electronic phase transition. Our results also show that when the Cr2N, inside the high-flux mixed film, is converted to CrN by annealing it inside NH3 environment at high temperature, the electronic phase transition is recovered. This strongly manifests the fact that phase pure and stoichiometric CrN films can show the metal-insulating electronic phase transition. The demonstration of the origin behind the controversy of the metal-insulator transition in CrN thin films marks significant progress for its potential applications in nanoscale devices [3,4,5].

gFigure Caption

Figure 1 (a) Low-magnification HAADF-STEM micrograph of the HCF film is presented that shows the presence of both Cr2N and CrN. Inset shows the EDP of the film with cubic [001] and hexagonal patterns. (b) STEM-EDS elemental maps corresponding to (a) show the spatial distribution and morphology of the Cr2N and CrN grains. (c) HAADF-STEM micrograph of the HCF film with bright regions that represent the Cr2N, while the darker parts showing CrN grains. (d) Cr, (e) N and (f) Cr+N STEM-EDS maps corresponding to the region (c) showing the different rains. (d) Cr, (e) N and (f) Cr+N STEM-EDS maps corresponding to the region (c) showing the different grains. (g) HAADF-STEM micrograph of the LCF film showing single-phase epitaxial single-crystalline CrN growth on MgO substrate. (h) Homogeneous and uniform Cr and N atomic distribution in the LCF film is demonstrated by the STEM-EDS map. (i) Atomic-resolution STEM image of the CrN/MgO interface from the LCF film is presented that exhibits cubic epitaxial CrN crystal growth on MgO substrate.

Graphic:



Keywords:

Chromiumnitrate, phase transition, STEM, EDS

Reference:

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[5] The authors acknowledge the facilities at Sydney Microscopy and Microanalysis at The University of Sydney.