

EELS Measurements and Ab-initio Calculations of the N-K Edge in TiN/VN Films Deposited on MgO Substrates

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Transition-metal nitrides may exhibit an unusual combination of physical and chemical properties such as high hardness and in case of formation of self-lubricious oxides due to oxidation of e.g. VN, low friction coefficients. Studying the surface and interface properties of well-defined TiN/VN layered coatings in terms of stability and electronic structure will provide the basis for a better understanding of microstructure-property relationships.

TiN/VN bi-layers were grown epitaxially on MgO (100) substrates using an unbalanced d.c. magnetron sputtering system at 580°C in a mixed Ar-N₂ atmosphere.

The electron energy-loss spectroscopy (EELS) measurements were performed with a JEOL 2010F and a JEOL 2100F operating at 200 kV, while the energy-loss near-edge structure (ELNES) of the N-K, Ti-L_{2,3}, and V-L_{2,3} edges was recorded in a 200 kV FEI TECNAITM F20 equipped with a monochromator [1, 2].

The electronic structure of TiN/VN bi-layers is calculated using the Vienna ab-initio simulation package (VASP) computer code, which uses density functional theory to describe the electronic interaction [3, 4].

TEM studies revealed that TiN/VN films grew with a cube-on-cube orientation relationship on the MgO substrates (Fig. 1) and possessed an interdiffusion zone of ~20 nm at the TiN/VN interface. EELS spectra recorded from the TiN and VN layers reveal some N deficiency with atomic ratios Ti/N of 1.1 ± 0.1 and V/N of 1.2 ± 0.1 . The ELNES of the N-K edges in TiN and VN, which have been acquired with ~ 0.2eV energy resolution, are shown in (Fig. 2). A comparison between theory and experiment for the N-K spectra prove that the effects of the core hole created in the excitation processes have to be included (Fig. 3). Both,

the position and relative heights of the calculated peaks agree best with full core-hole calculations. In VN the splitting of the N-K peak observed experimentally is smaller than the calculated one (Fig 3b), because of a significant number of N vacancies present in the VN film. The accommodation of vacancies (Fig. 3c) results in a peak broadening and shifting to higher energy and thus might serve as a fingerprint. The partial density of states for the N-K edge at TiN/VN interface (Fig. 3d) shows only little difference with respect to the bulk region. The experimental film did not contain a sharp interface as found by energy dispersive X-ray spectroscopy and EELS scans.

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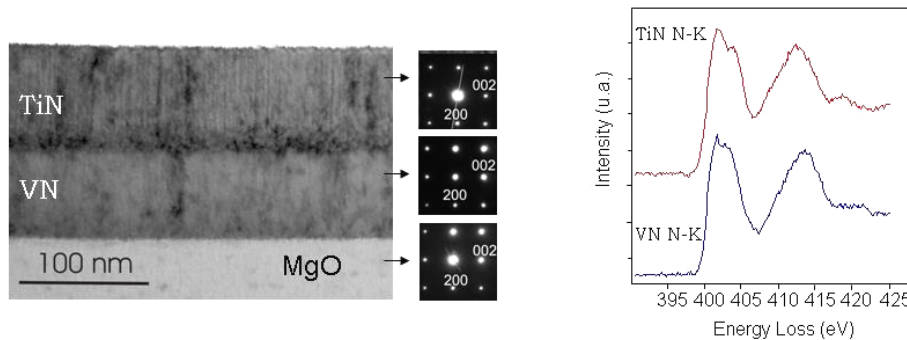


Figure 1: Bright-field TEM image of a cube-on-cube grown TiN/VN bi-layer deposited on a MgO (100) substrate.

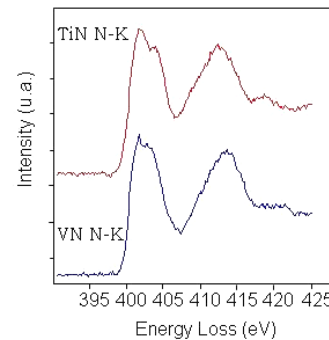


Figure 2: ELNES of the N-K edges of TiN and VN acquired with a monochromator.

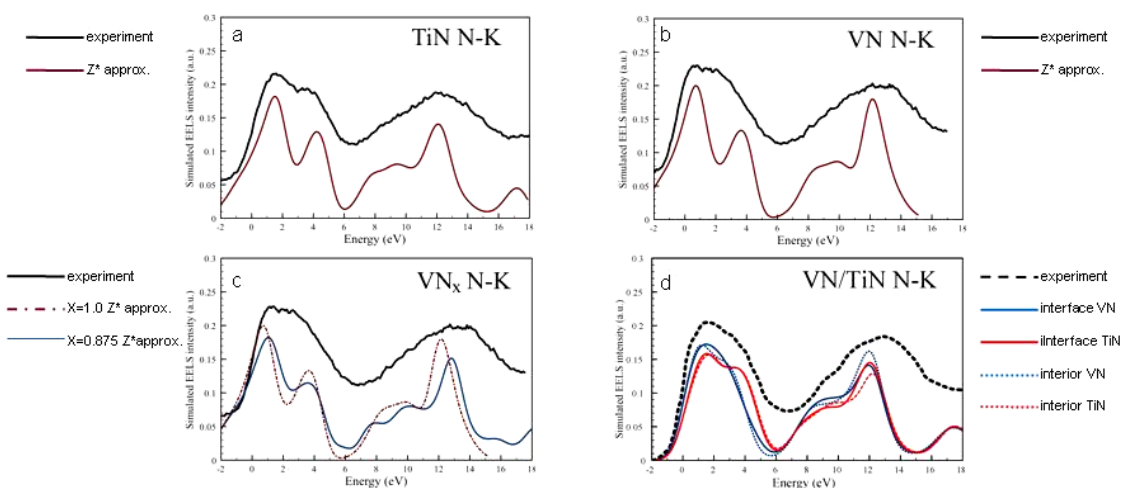


Figure 3: Comparison of the ELNES of the N-K edge in experimentally observed and simulated spectra: a) bulk TiN, b) bulk VN, c) bulk VN calculated with 12.5% nitrogen-deficiency and Ti-N stoichiometry, d) TiN/VN interface and bulk-like regions (interior of the slab without influence of surfaces and the interface) of the TiN and VN.