Transition metal nitrides have found wide-spread applications in the cutting- and machining-tool industry due to their extreme hardness, thermal stability and resistance to corrosion. The increasing demand of these nitrides requires an in-depth understanding of their structures at the atomic level. This has led to some experimental and theoretical research [1-6]. The films used in this study were deposited by reactive direct current magnetron sputtering of a Cr/V/Ti metal target in an Ar+N2 atmosphere at a constant total pressure of 1 Pa, a target power of 6 kW, and a temperature of 350°C. A TEM/STEM JEOL 2100F operated at 200 kV and equipped with an image-side CS-corrector was utilized.

We will present some recent results on the atomic and electronic structures of metal nitride thin films (CrN, VN and TiN) on MgO and Al2O3 substrates (Fig.1 and Fig. 2) using advanced TEM techniques, such as CS-corrected HRTEM/STEM, EELS/EDXS, quantitative atomic measurement and electron diffraction analysis as well as theoretical calculations. The atomic and electronic structures of interfaces are analysed and experimental and theoretical results compared in order to unveil interface induced phenomena between the nitride films and the oxide substrates [2,3].

Particularly, the study on the effect of N defects in a CrN film has led to some interesting conclusions. Ordered nitrogen (N) vacancies were often found to cluster at the {111} planes. Combining independent image analysis, such as atomic displacement/strain measurement using geometrical phase analysis, and spectrum analysis by examining the low loss and core loss, fine structure analysis, some generalized conclusions are drawn: (i) a relationship between the lattice constant and N vacancy concentration in CrN is established [5], (ii) the change of ionicity of the CrN crystal with the N vacancy concentration is shown; (iii) a relation between electronic structure change and elastic deformation in CrN films has been experimentally derived, revealing that the elastic deformation in CrN may lead to a noticeable change in the fine structure of Cr-L2,3 edge, i.e. L3/L2 ratio.

The effect of randomly distributed defects in the films has been explored in a quantitative way using quantitative electron diffraction, combined with HRTEM and EELS analysis. Quantitative electron diffraction analysis reveals that the intensity ratios of (111), and (200) reflections (I111/I200) sensibly varies with the defect densities. Some quantitative relations are established.


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Fig. 1: HRTEM image of the CrN/Cr interface, a defective layer between Cr and CrN originated from the ordered N vacancy.

Fig. 2: The anisotropic distribution of strain in the defective layer (exx).

Fig. 3: Diffraction pattern along [112] CrN and [0001] Al₂O₃ zone axis

Fig. 4: HRTEM image along [1-10] CrN and [01-10] Al₂O₃