

**STRUCTURAL HIGH TEMPERATURE INVESTIGATIONS OF
NANOCRYSTALLINE CHROMIUM-OXYNITRIDE THIN FILMS**

by

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This doctoral thesis attempts to explain some of the basic mechanisms of CrN thin film deposition and phase formation produced by reactive magnetron sputtering (PVD), as well as the description of thermally induced structural changes of the thin film phases by X-ray diffraction. Literature research documents the extensive publication effort by many well known authors in recent years, where respective aspects of the relationships between sputter parameter and material properties (i.e hardness) have been investigated only. This work present some of the main results regarding fundamental material properties of the system Cr-O-N and their structural changes as a function of temperature.

The aim of the experimental design of sample preparation has been the fact, that by altering two different energetic state variables (substrate temperature, electric sputter power), investigations on the interlink between phase formation and structural characteristics are possible. Since this information is not accessible during the deposition process directly, a work around – of introducing thermal energy to the system – enables investigational access to structural- and formational processes due to further thermodynamic activation. The gathered structural information allows a retrospective examination of the moment of deposition and initial formation.

In a first step, the method of HT-X-ray diffraction has been optimised in respect to temperature related high resolution experiments (5°C per scan) and their evaluation, to gather all structural changes at each temperature step within a reasonable amount of time (instrumental FWHM-contribution and HT-calibration with implementation of software aspects). The new capabilities of the Rietveld software TOPAS (©Bruker-AXS) have shown a tremendous increase of user friendliness as well as stable operation during refinement procedure. Additionally, the high convergence capability allows the simultaneous refinement of up to 85 HT-XRD scans.

First screening experiments have documented strong sample dependent limitations, like a low number of Bragg reflexes, deviated positions as well as broad FWHM. The evaluation of datasets before and after HT has proven a mismatch in peak profile description. Closer determinations have documented insufficient description of the X-ray datasets by the single phase structure model of CrN.

Since this peak description misfit could not be explained by using instrumental- or sample-defined aberrational functions either (i.e. X-ray source emission profiles; misalignment of the diffraction appliance; microstrain, strain, structural defects, texture), the effect of an additional phase contribution to the peak profile had to be considered, to describe the observed peak profiles sufficiently. This characteristic has been documented by the presence of an additional cubic structured phase beside CrN. Statistical tests of the refined lattice parameters have shown that these fit improvements are not significant to the calculated lattice parameter results. Nevertheless, successful double structure fit refinements have been proven to be the only possibility to document the presence of a multi phase composition by means of X-ray diffraction.

The chemical characterisation of these thin films by EPMA have indicated an enrichment of oxygen in samples of low sputter power. To understand this obvious kind of oxygen containing phase, considerations on the structural properties and probability are needed to establish working theories of its formation during sputtering and HT treatment. Literature research has documented only limited information on oxygen incorporations of Cr(N/O/#) solid solutions, nevertheless SUZUKI (2002; Thin Solid Films, 407, 118-121) postulates a $\text{Cr}(\text{O}_{0.46}\text{N}_{0.54})$ end member composition using a maximum concentration of oxygen < 46 at%, structurally isotyp to CrN (Fm-3m). Based on this literature, three model situations have been established. To understand the structural HT behaviour of the CrN thin films, considerations on the physical and chemical interaction between the different phases are necessary. All models include the recrystallisation of the CrN component as well as the formation of $\text{Cr}(\text{O}_{1-x}\text{N}_x)$ and $\text{Cr}_2(\text{N}_{1-x}\text{O}_x)_3$. This situation does not necessarily mean, that all three phases are present as chemically homogeneous and structurally individual crystallites, precisely separated by interfaces. However, more likely is a small number of coherent diffracting domains within one crystallite, characterised by individual chemistry and structure. Possibly covered by a thin oxide layer in nm- range. Nevertheless, it has not been clear, whether these domains are organised radial as a concentric shell model. These considerations have been confirmed by TEM investigations, where a homogeneous composition containing chromium, nitrogen and oxygen has been documented. EELS investigations proved the chemically and structurally bonding of oxygen to nitrogen, which evidences the existence of chromium oxynitride.

The investigation of the CrN lattice parameter has proven strong changes at HT (see Figure-1), which can be interpreted as increasing mobility of vacancies and unbound metallic chromium. The basis of this interpretation has been the chemical composition measured by EPMA analyses, where the results prove an over- or under saturated chromium concentration of the $\text{Cr}(\text{O}_{1-x}\text{N}_x)$ stoichiometry. For chemical compounds like CrN, the ratio has to be 1:1 for the cationic site as well as for the anionic site. This set-point deviation distinguishes, which model of defects can be applied.

For samples of low oxygen content (400W), a resulting Cr-concentration of approx. 54 at% has been determined. Due to this over-stoichiometric composition of chromium in the $\text{Cr}(\text{O}_{1-x}\text{N}_x)$ structure, the following defect-hypothesis-1 can be applied successfully; since nearly all available vacancies are anionic sites only, the relative quantity of chromium is over-stoichiometric. This apparent over-stoichiometry cannot be used to enable chromium mobility along the available vacancies, because of an electronic mismatch in charge. A high number of cationic vacancies would have enabled the mobility of chromium for diffusion towards the interface of the thin film, with a resulting oxidation to Cr_2O_3 . Since the samples of 400W show very low oxidation on the surface, the regarding defect-hypothesis-1 proves to be reliable.

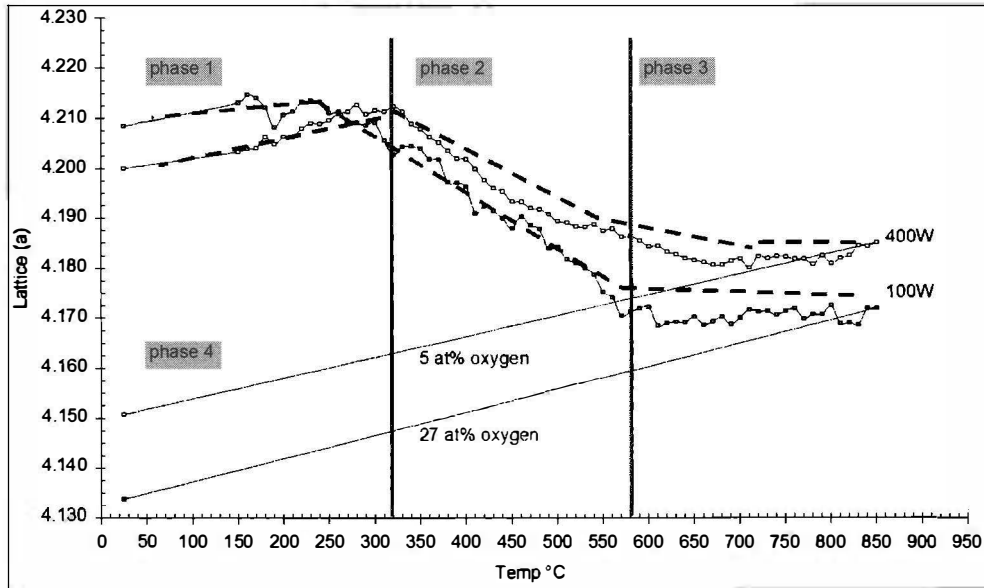


Figure 1

HT-XRD experiments of CrN 400W and 100W samples. Single values represent a statistical mean of 2 independent experiments. Experimental conditions: 25-90° 2Theta, 0.035 °/step, 2 sec/step, 10 °C/scan, 25°-850°-25°C, helium 5-9 atmosphere.

Samples of high oxygen concentration (100W; Cr-concentration of approx. 48 at%) must be described by a different model: ANDERSON (1965; "I- Electron Diffraction and II- The Nature of Defects in Crystals": Abstracts of Papers Presented at an International Conference, Melbourne, Australia, 16-21 August 1965 Canberra: Australian Academy of Science) postulates the variable distribution of defects in the anionic as well as the cationic sites for oxidic structures such as vanadium oxide. Due to the high oxygen concentration, although not determined by XRD, the 100W sample system can be possibly applied as a "semi-oxidic" system. This model is variable enough to describe the observed XRD data sufficiently: samples of high oxygen- and low chromium concentration (100W), show the largest spread of unit cell parameters within the first HT circle. This combination of different "cationic and anionic charged" vacancies (Schottky defects) and the resulting higher defect density, mobilises the chromium cations to the interface due to the input of thermal energy. This also explains the higher oxidation rate of these samples, as well as the wider spread in the contraction of the unit cell parameter, due to a large number of Schottky defects for the samples of 100W.

This work has documented the power of thermal structural characterisation successfully. Although the thin films are applied at high temperatures, very limited knowledge of this subject has been provided by literature regarding CrN thin films. It has further shown, that oxygen contamination realised as solid solution within the CrN structure, proves strong chemical activity in terms of mobility (vacancies, interstitials) and phase formation ($\text{Cr}(\text{O}_{1-x}\text{N}_x)$, Cr_2O_3 and unconfirmed $\text{Cr}_2(\text{N}_{1-x}\text{O}_x)_3$). To improve the oxidative stability of upcoming coating materials, further investigations on the structure of $\text{Cr}(\text{O}_{1-x}\text{N}_x)$ -solid solution and sputter energy are necessary to gain advanced knowledge.