

XPS investigations of chromium nitride thin films

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Abstract

Cr–N film coatings were prepared by magnetron sputter deposition at different nitrogen partial pressures. The film characterisation by XRD and DTG gives average bulk compositions of Cr₂N and CrN for the coatings. Highly sensitive XPS investigations were performed and the chemical and phase compositions of a film surface range of about 10 nm thickness was estimated quantitatively from the deconvoluted peak intensities. It is demonstrated that the composition of the surface of chromium nitride thin films differs from the core and is more complex in constitution. Not only chromium nitrides (Cr₂N and CrN) but also chromium oxynitrides and chromium oxides (CrO_x and CrO_xH_y) were detected. Metallic chromium was also found in films prepared at higher nitrogen flow. The concentration of the estimated phases shows dependence on film preparation and additional heat treatment.

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1. Introduction

Chromium nitride coatings were usually prepared by physical vapour deposition (PVD) techniques. The variation of the nitrogen pressure permits to produce films ranging in composition from mixtures of Cr and Cr₂N, pure Cr₂N through Cr₂N–CrN to pure CrN above all by increasing the nitrogen amount in the sputter chamber [1–3].

Chromium nitride coatings have achieved a great importance to reduce wear. Furthermore, chromium nitride films exhibit remarkable stability against oxidation and resist thermal heat treatment up to 600 °C. The oxidation rate is lower in comparison to other nitride hard coatings [4–16]. On the other hand, the surface region of chromium nitride coatings can be converted to oxygen containing phases already at ambient temperatures, which should influence the properties of coated tools.

The presented X-ray photoelectron spectroscopy (XPS) investigations were performed in order to obtain quanti-

tative results about the surface composition from different chromium nitride coatings. We will demonstrate that beside formed oxides, further phases in the surface region have to be considered.

2. Experimental

For the coating deposition a PVD magnetron sputter unit Alcatel SCM 601 with r.f. bias was used. The Cr–N composition was controlled by the N₂ reactive gas flow. Chromium nitride coatings were deposited on thin metal substrate sheets of about 12 cm in diameter from which they could be removed for further investigations by scraping off. Four different specimens (samples 1–4) were prepared in different nitrogen reactive gas flow of 3.5, 4, 12.5 and 18 sccm. The film surface (annex a to sample number) and the former film–substrate interface (annex b) of the specimen were investigated. A series of samples was heat treated at temperature up to 530 °C in a tube furnace in nitrogen atmosphere.

The film morphology and thickness was investigated by SEM, using a Hitachi S400. An X-ray examination was performed with Seifert XRD 7 spectrometer and the phase composition was determined. The chemical compo-

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sition was obtained by a thermal gravimetric experiment using a thermo analyser Seteram TGS 92. The samples were heated up to 1600 K and the mass increase was measured [17].

The XPS investigations were performed with VG ESCALAB 200 X electron spectrometer. Binding energy data were referenced to the aliphatic C 1s peak at 284.8 eV. The spectrometer energy scale was calibrated following ISO 15472 [18]. Sample fragments of the coating of 4 × 5 mm size were put on an adhesive tape. The determination of the element concentration was done under the assumption of a homogeneous distribution in the analysed volume (1 mm diameter and 10 nm depth). The UNIFIT2004 software (R. Hesse, Uni Leipzig) was used for XP spectra analysis and for quantitative routine the respective VG ECLIPSE data system. The estimation of the relative intensities (atomic ratios) and surface concentrations (in atomic percent) was performed using Scottfield's cross-sections [19], inelastic electron mean free path lengths $\sim E_{\text{kin}}^{0.7}$ and a transmission $\sim E_{\text{kin}}$ (CRR10 analyser mode). The uncertainty of the atomic ratios is estimated to be better than $\pm 10\%$.

3. Results and discussion

The films investigated have a thickness of about 3 μm . The morphology of the former interface between metal substrate and first deposited chromium nitride reflects the surface structure of the substrate metal. The external surface of the deposited coating has a granular structure. The crystalline phase composition of the film material investigated by XRD yields Cr, Cr₂N and CrN. The thermal analysis indicates a weight increase above 550 °C. This is connected with the complete oxidation of the nitrides and the formation of Cr₂O₃, which was confirmed by the XRD results. Thus chemical compositions of Cr₂N_{0.92} for the samples 1 and 2 and of CrN_{1.007} for the samples 3 and 4 were estimated.

The XPS investigations of the surface of the Cr–N films show the presence of the elements Cr, N, O and contaminations of C and Si. Iron can be detected on the internal surface, the former interface between the metallic substrate and the growing chromium nitride film. From the intensity of the Cr 2p, N 1s, O 1s and Fe 2p peaks a coating composition was estimated. For this, it was assumed that carbon and the corresponding oxygen belong to a contamination layer. The oxygen content was reduced in connection to the iron content in a relation of Fe: O = 1:1.5 (Fe₂O₃). The results are given in Table 1. The internal coating–substrate interface contains significant higher oxygen and lower nitrogen amounts. This can result from the presence of oxygen in the plasma during the starting period of precipitation. The peaks of chromium Cr 2p, nitrogen N 1s, oxygen O 1s and carbon C 1s were investigated in detail and peak position and

Table 1

Chemical composition of the surface region of Cr–N films in atomic percent (at.%)

Spectra	Samples							
	1a	1b	2a	2b	3a	3b	4a	4b
Cr 2p	48	35	51	48	43	40	39	30
N 1s	13	6	19	12	35	17	42	12
O 1s	39	59	30	40	22	43	19	58

a—external film surface; b—coating–substrate interface.

intensity were estimated. Each spectrum was fitted by least square method using Gaussian–Lorentzian envelope. The deconvolution of the peaks gives three to four features (see Fig. 1). These features were assigned to element species in different chemical bonding to their neighbours.

The deconvoluted chromium peak was taken with 4 groups of different chemical species: metallic chromium Cr⁰ (574.3 ± 0.4 eV [20]), chromium in nitrogen environment (CrN, Cr₂N, CrN_xO_y, 575.7 ± 0.4 eV [21,22]), oxidic or hydroxydic Cr^{III} (Cr₂O₃, Cr(OH)₃, CrO(OH), 576.8 ± 0.4 eV [20,23,24]). The peak at 578.3 ± 0.4 eV is assigned to CrO₃ [25] or many-body interactions [26]. The co-existence of Cr^{III} and Cr^{VI} in partly oxidised chromium nitride films was also observed by other authors [9].

The N 1s peak can be composed by five species due to chromium nitrides (396.8 ± 0.4 eV for CrN [21] and 397.4 ± 0.4 eV for Cr₂N [21]) mainly and different chromium oxynitrides (398.2 ± 0.4 eV). The smaller peaks at 399.4 ± 0.4 eV and 401.9 ± 0.4 eV occur in chromium nitrites/nitrates [27].

The oxygen peak O 1s gives four species indicating the presence of Cr₂O₃/CrO₃ (530.0 ± 0.4 eV [20]/529.7 ± 0.4 eV [25]), Cr(OH)₃/CrO(OH) (530.8 ± 0.4 eV [23]/531.4 ± 0.4 eV [24]), and (532.0 ± 0.4 eV or 533.0 ± 0.4 eV) in organic compounds, silicon oxide and water.

The intensity of the sub-peaks of the deconvoluted chromium Cr 2p peak can be used for an estimation of the amounts of different chromium phases in the surface range. With increasing nitrogen flow during film preparation, the concentration of CrN increases from 25% to 45% and the amount of metallic chromium decreases from 45% to 25%, whereas the concentration of Cr₂O₃ and CrO₃ of about 30% remains constant (see Fig. 2a).

The analysis of the N 1s peak gives a distribution of Cr–N compounds. The samples prepared at low nitrogen flow contain CrN, Cr₂N and Cr(O, N)_x. The amount of CrN increases with increasing nitrogen flow. On the other hand the content of Cr₂N and Cr(O, N)_x decreases and the concentration of chromium nitrite remains constant below 10% (see Fig. 2b).

From intensity of the peaks of Cr 2p, N 1s and O 1s a coating composition was evaluated. Here only the intensities of the oxygen species at ~530 and ~531 eV were considered. The results are collected in Table 2. A

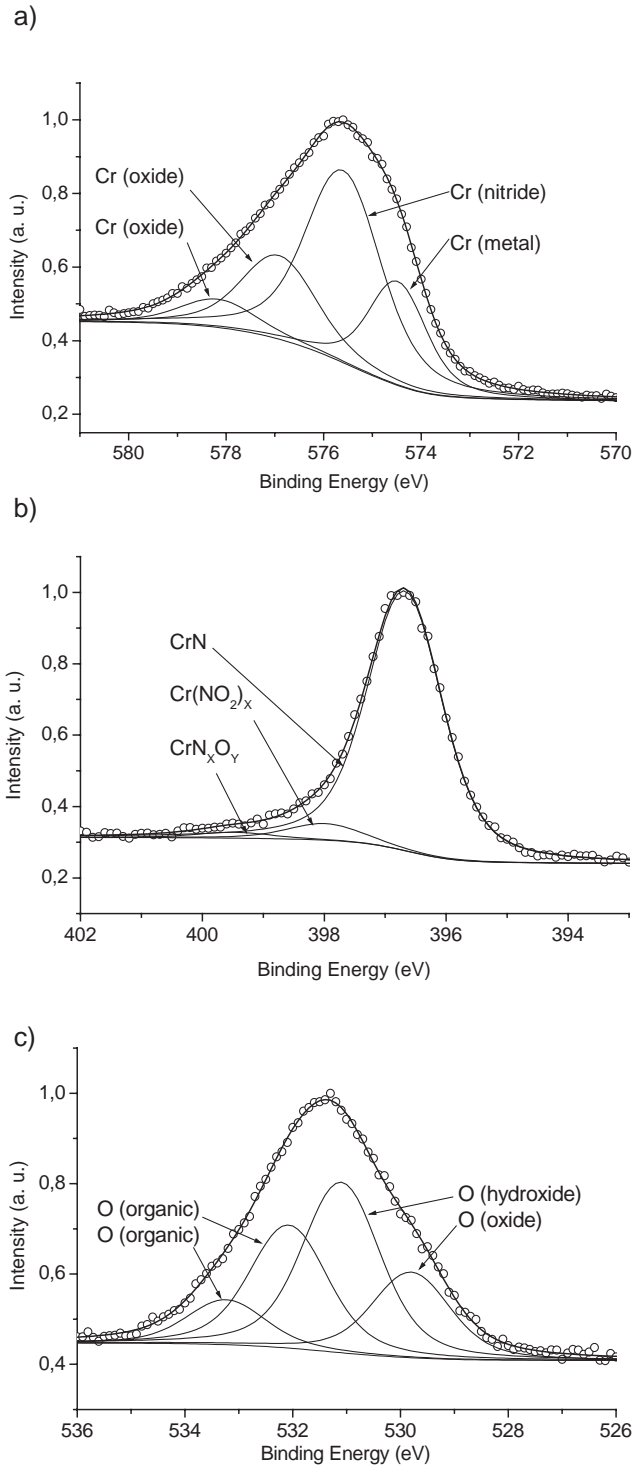


Fig. 1. XPS peak Cr 2p (a), N 1s (b), and O 1s (c) of sample 3.

different coating composition, in comparison, between the internal and external surface of the films was observed. The interface where the film growing started has a higher oxygen concentration of about 50–60 at.% and a very low nitrogen amount of about 10–15 at.%. The external surface contains about 50 at.% chromium. Whereas the chromium concentration remains relatively constant, with

increasing nitrogen flow in the precipitation chamber the nitrogen amount in the coating increases to 40 at.%. A heat treatment at 530 °C has a significant influence on the coatings prepared at low nitrogen flow. The chromium nitride and the metallic chromium disappear in these samples and instead of them chromium oxide was built. Obviously, these films are more thermally unstable in comparison to the films of higher nitrogen content, where still about 45 at.% CrN and 20 at.% Cr can be detected.

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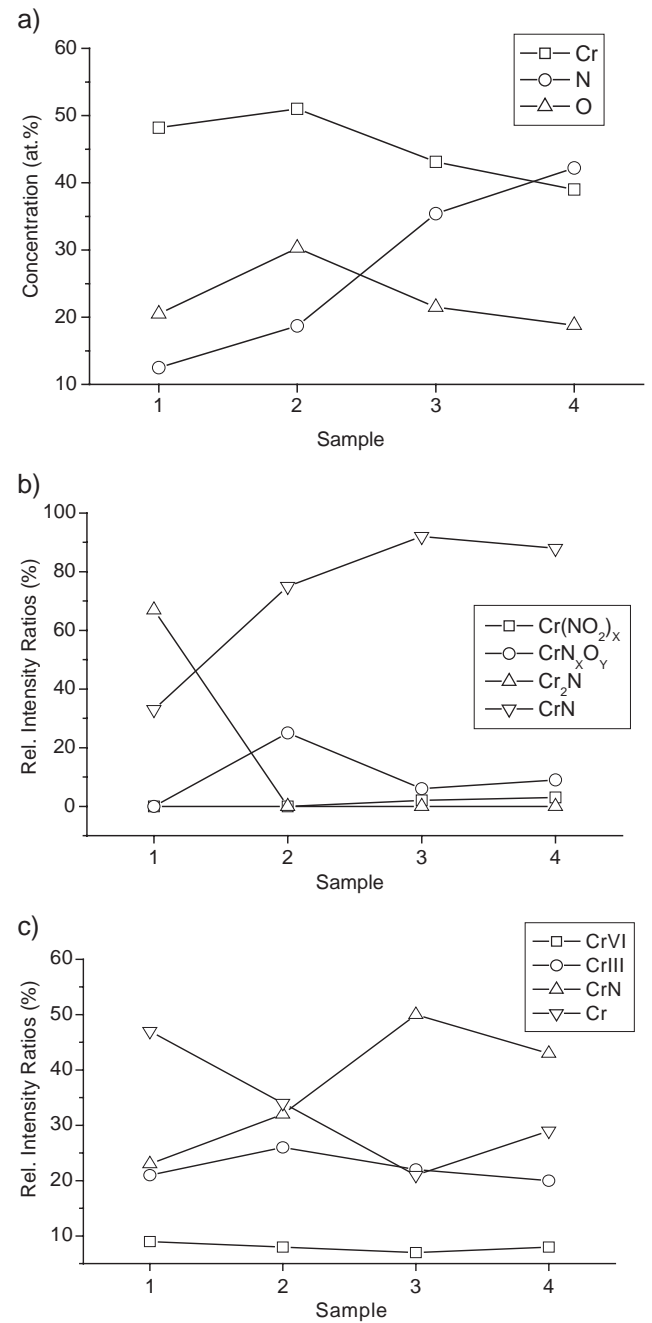


Fig. 2. Film surface composition: intensity ratios of chromium (a), intensity ratios of nitrogen (b), and atomic ratios of Cr, N, and O (c).

Table 2
Phase composition of the surface region of Cr–N films in percent (%)

Phase	Samples							
	1a	1b	2a	2b	3a	3b	4a	4b
Cr ₂ N	15	0	0	0	0	0	0	0
CrN	10	15	20	15	45	35	40	40
CrO _x N _y	0	10	10	20	5	5	5	5
Cr	45	30	35	35	20	30	30	5
Cr _x (NO ₂) _y	0	0	0	0	<5	<5	<5	5
CrO _x +CrO _x H _y	30	45	35	30	30	30	25	45

a—film surface; b—film–substrate interface; uncertainty ± 5%.

The results show that all samples contain more or less chromium oxide and metallic chromium in the surface region. The obtained surface composition should be influenced not only by the film preparation conditions but also by a decomposition of the Cr₂N and an oxidation at room temperature and according to



that was also noticed after the annealing at 530 °C. It is assumed that the oxide or the oxynitrides species observed form a thin layer, which evidently inhibits further oxidation at room temperature [7].

4. Conclusions

The surface composition of Cr–N coatings, prepared at different nitrogen flows, is more complex in composition in comparison to the core. Additionally to Cr₂N and CrN, metallic Cr and oxygen containing phases like Cr(O,N)_x, CrO_x and CrO_xH_y were detected in all samples. A quantitative estimation of the present phases in the surface of the Cr–N coatings of different bulk compositions can be given. The difference between the composition of surface and substrate–coating interface was demonstrated. The interface contains less nitrogen and more oxygen. A heat treatment at 530 °C of the films results in decomposition of Cr₂N and oxidation of the metallic chromium, whereas the film core remains still unaffected. It is concluded that metallic chromium and the oxide phases are produced not only during the sputter process. The metallic chromium and the oxides are also a result of the decomposition and oxidation of the nitrides at ambient temperatures. The surface reactivity of the coatings at room temperature anticipates the oxidation reaction mechanism of the core at higher temperatures. But the oxidation reaction at ambient

temperature is very slow because of the low diffusion rate of the chromium ion through the oxide layer as the limiting step.

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