Tuning the crystallographic and electronic properties of chromium oxynitride films

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Nitrides and oxides of chromium exhibit substantial differences in their crystallographic and electronic structure. The present study shows some of the possibilities for tuning the crystallographic and electronic properties of chromium oxynitride films by progressively increasing the oxygen concentration. We observe that upon oxygen addition the $\text{CrO}_x\text{N}_{1-x}$ films remain in the face centered cubic B1 structure of CrN, up to oxygen contents of $x \leq 0.70$. At higher oxygen concentrations they gradually adopt the properties of chromium sesquioxide and crystallize in the corundum Cr_2O_3 structure. The gradual decrease of the stress-free lattice parameter of the films with the B1 structure indicates that oxygen substitutes progressively for the nitrogen atoms. The (001) preferred orientation of the B1 films becomes more pronounced with the increase of oxygen concentration in the films. This trend is ascribed to the increased energy of the polar (111) planes with the substitution of nitrogen by the more electronegative oxygen anions. Changes in the core-level binding energies (BE) of the Cr $2p_{3/2}$ and N $1s$ observed by X-ray photoelectron spectroscopy (XPS) with increasing x indicate enhanced charge transfer from Cr to O with respect to N. A shift of the valence band edge toward higher BE suggests a decrease of electrical conductivity of the films with increasing oxygen content. © 2011 American Institute of Physics. [doi:10.1063/1.3549115]

I. INTRODUCTION

The capability to design novel nonequilibrium solid structures using thin film technologies has boosted in recent years the growth and practical use of a wide variety of 3d transition metal (TM) nitrides,^{1–3} oxides,^{4–10} and oxynitrides.^{11–13} This interest has triggered numerous efforts to investigate their electronic and crystallographic structure and consequently their potential for applications. As a consequence of their high electronegativity, nitrogen and oxygen have a strong tendency to attract electrons from neighboring metal atoms, creating strong crystal fields which result in metallic, semiconducting, or insulating behaviors such as those, for example, in ZrN, CrN, and Cr_2O_3 films, respectively. Similarities between crystallographic and electronic properties of nitrides and oxides enable the formation of mixed compounds like oxynitrides or carbonitrides. This variability makes them of great practical value in different fields such as microelectronics,^{14,15} heterogeneous catalysis,¹⁵ superconductivity,¹⁵ protective coatings,^{11–13} and magnetism.¹⁶ Knowing the phase regimes and understanding the role of nitrogen and oxygen in oxynitride films is therefore crucial to understanding the properties of this class of compounds. Cubic nitrides of several TMs, such as TiN, CrN, VN, and ZrN, are thermodynamically stable,¹ while the corresponding monoxides are unstable and, hence, it is not possible to obtain them in the bulk form. The main reason for

this instability with respect to the corresponding nitrides is the destabilizing effect of occupied antibonding orbitals when going from nitrides to oxides.^{7,8,10} The electrostatic repulsion of the directed oxygen e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) in TM octahedra leads to the distortion of the octahedral symmetry in B1 nitrides and to the energy splitting of the e_g and t_{2g} orbitals, known as the Jahn–Teller effect.¹⁷ A way to stabilize TM monoxides is the formation of ordered nonmetal vacancies in B1 structures, whose concentration may be as high as 25%. The consequent distortion of the B1 lattice results in crystallization of oxides in lower symmetry structures; monoclinic for Ti and V,^{1,9} or orthorhombic for Cr.¹⁰ This holds especially true for Cr because of its nearly half-filled d band.^{7,9,10} It has been shown that metastable, ultrathin CrO films of 1–3 monolayers (ML) with a B1 structure can be deposited. These monolayers are stabilized by vacancies due to the reduced bond energy in the basal planes.^{7,8} It was shown that 20–30% of the metal positions in the B1 CrO lattice of these films are vacant, with the energy of the oxide destabilized by the occupation of the antibonding orbitals.^{7,8} The cumulative effect of the antibonding orbitals, becoming more prominent as the thickness of chromium oxide exceeds about three ML, results in a loss of structural stability and, thus, the material will transform into the thermodynamically stable Cr_2O_3 with corundum structure. A further reason for the impossibility of forming stable CrO seems to be the fact that Cr^{2+} ions are unstable in the presence of oxygen, in contrast to Cr^{3+} that forms stable oxides. The metal in a hypothetical CrO should then be Cr^{3+} ions. In fact, previous

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attempts to obtain B1 CrO thin films^{7,8,10} failed due to the necessary formation of Cr vacancies with a concentration of ~20–30%, similarly to other defective TM monoxide films such as TiO (see Refs. 4 and 9), MnO, and VO (Ref. 9). In addition to the structural differences, chromium nitrides and oxides exhibit also substantially different electronic properties. CrN thin films are semiconductors ($\sim 5.5 \times 10^1 \text{ S cm}^{-1}$ at room temperature)¹⁸ with a bandgap of 71 meV,¹⁸ while Cr₂O₃ is an insulator with a conductivity a factor 10^8 lower ($\sim 1.8 \times 10^{-7} \text{ S cm}^{-1}$ at room temperature)¹⁹ and a bandgap of 4.8 eV (Ref. 20). In films deposited by a highly nonequilibrium process, such as cathodic arc evaporation, the formation of metastable solid solutions has to be considered.²¹ For example, Ürgen et al. have recently reported a phase stability of the B1 structure in CrO_xN_{1-x} up to 46% of oxygen,¹² while in our previous study¹³ we observed the B1 structure in chromium oxynitride films up to an oxygen content of 70%. The aim of the present work is to investigate the effect of the oxygen and nitrogen content on the crystal structure and the electronic properties of CrO_xN_{1-x} thin films in the full range of oxygen concentrations from 0 to 100%.

II. EXPERIMENTAL

CrO_xN_{1-x} coatings were deposited in OC Oerlikon Balzers industrial deposition plant by reactive cathodic arc evaporation. The coatings were grown to a thickness of 4–8 μm on mirror polished WC-Co cemented carbide substrates. Prior to deposition the substrates were ultrasonically cleaned and dried with pressurized air. The depositions were carried out at a total pressure of 3.5 Pa which was kept constant by adjusting the flow of N₂ (ΦN_2) and O₂ (ΦO_2) and controlling the pumping power with a standard regulation valve, while their ratio was kept constant during each growth. The flow ratio was varied from 0 to 1, as shown in Table I. The deposition temperature was $T_s = 480^\circ\text{C}$ and the negative bias voltage was 50 V. The chemical composition of the coatings (see Table I) was determined by X-ray photoelectron spectroscopy (XPS) using a PHI Quantum 2000 XPS system. The system was operated using monochromatized Al K α radiation. The coatings, showing some surface roughness typical for films prepared by arc evaporation, were mirror polished

TABLE I. Sample designation, O₂ and N₂ gas flow (sccm), relative gas flow ratio $\Phi\text{O}_2/(\Phi\text{O}_2 + \Phi\text{N}_2)$, values of relative oxygen content $x = \text{O}/(\text{O} + \text{N})$, composition, and structure of CrO_xN_{1-x} coatings

Sample designation	O ₂ flow	N ₂ flow	$\Phi\text{O}_2/(\Phi\text{O}_2 + \Phi\text{N}_2)$	x	Composition	Structure
A	0	1200	0	0	CrN	B1
B	50	1150	0.04	0.27	CrO _{0.27} N _{0.73}	B1
C	100	1100	0.08	0.44	CrO _{0.44} N _{0.56}	B1
D	150	1200	0.11	0.48	CrO _{0.48} N _{0.52}	B1
E	150	1000	0.13	0.55	CrO _{0.55} N _{0.45}	B1
F	200	1050	0.16	0.70	CrO _{0.70} N _{0.30}	B1
G	250	1100	0.19	0.97	Cr ₂ (O _{0.97} N _{0.03}) ₃	corundum
H	300	875	0.26	1.00	Cr ₂ O ₃	corundum
I	400	0	1.00	1.00	Cr ₂ O ₃	corundum

with 1/4 μm diamond paste before XPS analysis to minimize alterations due to the surface topography.²² The concentration values were obtained after Ar⁺ sputter cleaning at 1 kV, corresponding to a removal of 10 nm of carbon. The binding energy scale was referenced to the C 1s peak position at 284.5 eV to be independent of electrostatic sample charging effects. The uncertainty of the binding energy values is estimated to be ± 0.25 eV, given by the chosen step size. Preferential sputtering and the higher oxygen content close to the surface of the films leads to an uncertainty in the relative oxygen concentration $x = \text{O}/(\text{N} + \text{O})$ of ± 0.05 , as estimated from a set of comparison analyses performed by Rutherford backscattering spectroscopy. The electronic properties in terms of core-level electron binding energy were investigated using the position of the Cr 2p, N 1s, and O 1s bands. The elemental concentrations were evaluated using the built-in sensitivity factor of the spectrometer after a Shirley background correction.²² The XPS valence band edge has been estimated from the intersection of the linear fit of the edge with the background. The phase composition and preferred orientation of the CrO_xN_{1-x} films were investigated by XRD using an X'Pert Pro MPD Panalytical powder diffractometer with a standard Bragg–Brentano geometry and Cu K α radiation. The crystallographic preferred orientation of the grains was estimated by calculating the Harris texture coefficient²³

$$T_{hkl} = \frac{I_{hkl}/I_{h'k'l'}}{\frac{1}{n} \sum I_{hkl}/I_{h'k'l'}},$$

where I_{hkl} is the measured intensity of the (hkl) diffraction peak and $I_{h'k'l'}$ is the correspondent relative peak intensity obtained from an ideally randomly oriented material as described in the Joint Committee Powder Diffraction Standard (JCPDS) database for random powder samples. Further experimental details on the CrO_xN_{1-x} films were given in a previous study.¹³

III. RESULTS AND DISCUSSION

A. Composition and crystal structure

At a constant total pressure and pumping speed in the deposition chamber, the partial pressures of O₂ and N₂ are related to their relative flow ratios $\Phi\text{O}_2/(\Phi\text{N}_2 + \Phi\text{O}_2)$. As a consequence of the higher reactivity of O₂ than N₂ with Cr, the competitive reaction of N₂ and O₂ with the metal results in an increase of the oxygen content x in CrO_xN_{1-x} films up to 1.00 only for $\Phi\text{O}_2/(\Phi\text{N}_2 + \Phi\text{O}_2) > 0.20$, as shown in Fig. 1. The absolute value of ΔG^f of Cr₂O₃, the most stable chromium oxide, is approximately ten times higher than that of CrN (Ref. 24), calling for the preferential formation of Cr₂O₃ over that of CrN. However, below a flow ratio value of about 0.15 the layers crystallize in the B1 lattice of CrN with x up to 0.7. Under nonequilibrium conditions (typical in a nonthermal plasma process) thin film growth is determined by kinetics rather than by thermodynamics. Relatively high values of $\Phi\text{N}_2/(\Phi\text{N}_2 + \Phi\text{O}_2)$ —which cause a greater collision frequency of N₂ with Cr atoms on the growing surface than O₂—lead to the formation of a CrN and thereby

FIG. 1. Dependence of the oxygen fraction $x = O/(N + O)$ of the CrO_xN_{1-x} coatings on the gas flow ratios $\Phi O_2 / (\Phi N_2 + \Phi O_2)$.

stabilize the less stable nitride, despite the presence of oxygen. The formation of mixed chromium oxynitride at $\Phi O_2 / (\Phi N_2 + \Phi O_2) < 0.20$ must therefore be attributed to kinetic effects, i.e., the higher collision frequency of N_2 with Cr during the growth.

In this kinetic-thermodynamic competition, kinetics prevail for oxygen contents up to $x \leq 0.70$, as the films crystallize in the B1 structure of CrN, despite the fact that B1 CrO does not exist in bulk form. The XRD patterns of the CrO_xN_{1-x} coatings, evidencing this finding, are shown in Figs. 2 and 3. The corresponding structure and composition as a function of oxygen content are summarized in Table I. The presented data include diffractograms from our previous work,¹³ along with new data for $x = 0.27, 0.48, 0.55$, and

FIG. 2. X-ray diffractograms of the B1 CrO_xN_{1-x} films with different oxygen content x .

FIG. 3. X-ray diffractograms for the corundum-type $Cr_2(O_xN_{1-x})_3$ films with different oxygen content x .

1.00 (samples B, D, E, and H respectively). The diffractograms show three different trends as a function of the oxygen content x : a gradual peak broadening, shift of the diffraction peaks, and a change of the crystallographic texture. The broadening and shift of the diffraction peaks was attributed in our previous study¹³ to a change in the grain size and to substitutional incorporation of the oxygen on the nitrogen sites within the B1 unit cell, which results in a decrease of the stress-free lattice parameter. The texture evolution observed in the XRD patterns is discussed in the present work.

For $x > 0.70$ the films crystallize in the Cr_2O_3 corundum structure. As can be seen from Fig. 3, the diffraction peaks exhibit a slight shift toward higher diffraction angles at high values of x , indicating a decrease of the interplanar spacing. Additionally a change in their relative intensity with increasing x from 0.97 in $Cr_2(O_{0.97}N_{0.03})_3$ to 1.00 in Cr_2O_3 is observed. The larger unit cell in the $Cr_2(O_{0.97}N_{0.03})_3$ is attributed to the incorporation of N into the Cr_2O_3 corundum structure, as the Cr-N bond in CrN (2.06 Å) is longer than the Cr-O bond in Cr_2O_3 (2.01 and 1.96 Å).²⁵

Let us now consider the coatings with the B1 structure. As mentioned above, the XRD patterns shown in Fig. 2 exhibit three significant trends: a broadening and a progressive shift of the diffraction peaks toward higher 2θ angles and the development of a strong (002) preferred orientation. The shift of the diffraction peaks can be caused by the residual stress in the coatings and by the possible incorporation of O into the B1 CrN structure. In an earlier study on the same coatings,¹³ the stress-free lattice parameter a_0 was determined using the $\sin^2\psi$ method. These values were compared to the expected trend for the substitutional incorporation of oxygen using Vegard's law.²⁶ The Vegard line was calculated using the theoretical lattice parameter $a = 4.08$ Å for B1 CrO proposed by Schmid.⁷ As shown in our previous study,¹³ the data points close to the Vegard line indicate that O substitutes progressively for N in the B1 structure. A

FIG. 4. Texture coefficient T_{hkl} vs the oxygen content x of the samples with the B1 structure calculated from the (002) and (111) diffraction peaks.

further support of this interpretation is given by the evolution of the crystallographic preferred orientation of the coatings presented in Fig. 4. As can be seen, the value of T_{002} increases with increasing x , while T_{111} exhibits the opposite trend. To understand this development we have to consider that several factors influence the preferred orientation in polycrystalline thin films: the type of substrate, the deposition rate, the substrate temperature T_s , and the bias voltage are among the most important ones.²¹ The random grain orientation of the polycrystalline WC-Co cemented carbide substrate rules out epitaxial relations with the substrate as a cause for the texture evolution of the coatings, as this would lead to a random film grain orientation. Moreover, if the substrate determined the texture, no texture evolution would be observed with x , which is clearly not the case. The deposition rate of the $\text{CrO}_x\text{N}_{1-x}$ films was approximately constant (~ 1.2 nm/s) in the whole $\Phi\text{O}_2/(\Phi\text{N}_2 + \Phi\text{O}_2)$ range, and values of T_s and the bias voltage were the same for all depositions. Therefore, none of these three parameters can account for the observed changes.

Another reason may lie in the crystallographic properties of the B1 structures: the texture evolution of the films can be ascribed to the change of surface energy of the different crystallographic planes as the composition, given by x , changes. The polarized (111) planes of the B1 structure represent a periodic alternating sequence of cationic and anionic surfaces.^{3,27} Conversely, the (001) planes are neutral due to the presence of ordered anions and cations on the surface, which mutually balance their electronic charges. For this reason, the (001) planes of TiN exhibit a lower energy than the (111) planes.³ With increasing electronegativity of the anion, which occurs with the substitution of N by O, the dipole interactions between oppositely charged (111) planes increases, while the (002) family of planes remains neutrally charged. The energy difference between the two families of planes should therefore increase. Consistently, theoretical studies²⁷ proposed that the (111) planes in CrO with B1 structure are thermodynamically unstable with a surface potential divergent to infinite due to the $\text{Cr}^{2+}/\text{O}^{2-}$ planes with a net dipole moment parallel to the surface normal. Consequently, the (001) planes of the hypothetical cubic

FIG. 5. Cr 2p, N 1s, and O 1s XPS peaks of the $\text{CrO}_x\text{N}_{1-x}$ films with $x = 0.27, 0.70$, and 1.00 (samples B, F, and I, respectively).

CrO are the only stable planes. Thus, the sharp increase of T_{002} with increasing x is consistent with the progressive formation of B1 CrO.

B. XPS investigations

To obtain information on the chemical environment of the involved elements, XPS investigations on the $\text{CrO}_x\text{N}_{1-x}$ coatings were performed. The core-level spectra of Cr 2p, N 1s, and O 1s are shown in Fig. 5, while Fig. 6 shows the corrected binding energy (BE) and the full width at half maximum (FWHM) of these peaks. It is evident that the FWHM of the Cr $2p_{3/2}$ peaks is significantly larger than that of the N 1s and O 1s peaks due to the overlapping of several states, including the two spin-orbit components and the presence of a charge-transfer screened satellite peak at higher BE. The changes in the width of a core-level peak reflect variations in the chemical environment of the investigated element.²⁸ The observed variation of the FWHM of the O 1s peak as a function of x suggests that the addition of oxygen enriches the complexity of the chemical states in the analyzed films. Small changes are observed in the FWHM of the Cr $2p_{3/2}$ peaks, which increases up to $x \sim 0.40$ and then remains constant. The structural complexity increases markedly in the transition from the B1 to corundum structure. The increase up to $x = 0.5$ is due to the increasingly random surrounding of Cr by O and N. The plateau for $0.5 < x < 0.7$ is a consequence of the changed coordination of Cr by oxygen and nitrogen. The plateau above $x = 0.7$ is due to the complex environment of Cr atoms in the corundum structure, which exhibits two different Cr-O bond lengths (1.964 and

FIG. 6. Cr $2p_{3/2}$, N 1s, and O 1s peak positions (left) and the full width at half maximum (FWHM, right) of the XPS peaks of the films as a function of the oxygen content x .

2.013 Å) and four different O-Cr-O angles between 81.4° and 99.0° (see Refs. 25 and 29).

The FWHM of the O 1s peak increases up to $x \sim 0.55$ and then decreases for higher x . The FWHM at $x \sim 0.5$ is markedly larger than that at $x = 1$, which is indicative of the presence of at least two chemically different states. These are very probably those of O in a CrN-dominated surrounding (B1 structure) and those of O in the Cr_2O_3 structure that overlap in the regime between $x = 0.25$ and 0.7. Conversely, the N 1s peak width remains constant until $x \sim 0.55$ and then exhibits a slight broadening for larger x . This evolution reflects the increased diversity of chemical environments of nitrogen as more oxygen atoms are randomly incorporated into the lattice at higher x . The minute broadening of the N 1s peak is typical for disorder broadening.³⁰

The value of the Cr $2p_{3/2}$ binding energy for $x < 0.6$, is close to that of CrN (Ref. 2) and then increases, crossing the value of CrO (Ref. 5) between 0.55 and 0.70. It finally reaches the value typical for Cr_2O_3 above $x \sim 0.70$ (Ref. 6). The progressive increase of the Cr $2p_{3/2}$ BE is in good accordance with the gradual substitution of nitrogen by oxygen. The higher charge transfer between Cr and O, as compared to less electronegative N, results in the observed shift to higher BE.²² The N 1s BE remains constant at the value of CrN (Ref. 2) for $x \leq 0.55$ and then slightly increases. The formation of bonds between N and O can be excluded since the BE of the N 1s in nitrates is higher than 400 eV, while the observed BE peak positions observed here are more than 3 eV lower. The slight increase of the N 1s BE by about 0.25 eV may be due to the backflow of electron density from N to Cr, which itself is positively charged by the electron density depletion caused by the highly electronegative O. These results confirm the finding mentioned above that N is directly bonded to Cr. Similarly, the O 1s

peak position is constant until $x \sim 0.55$, and then increases up to the typical value for Cr_2O_3 (Ref. 6). A chemical shift of the O 1s peak toward lower BE is expected as a consequence of charge transfer from Cr to O. Instead, an increase of the O 1s binding energy is observed. In this case other factors seemingly affect the BE chemical shifts, such as a change of the Madelung energy or screening effects due to electronic relaxation phenomena.^{24,31–33} Such trends are not uncommon, as they have been observed both in Cr and Pb oxides.^{31,33} The change of BE observed in our samples starts when they still have the B1 structure, therefore the Madelung energy has a negligible effect on these BE shifts. This is in fact seen in Fig. 6, as the BE of O 1s remains constant as long as the coatings crystallize in the B1 structure; it increases only when the structure and the electric conductivity change from conductive CrN to insulating Cr_2O_3 . Accordingly, the change of conductive properties observed in previous studies^{12,19} seems to be consistent with the evolution of the valence band (VB) structure, which is shown in Fig. 7 and discussed below. We therefore assume that diminished core-level screening is the main effect causing the increasing binding energy of the O 1s peak.

The electronic stabilization of the B1 CrO with N up to a critical concentration of $\text{N}/(\text{O} + \text{N})$ close to ~ 0.20 – 0.30 (i.e. $x \sim 0.80$ – 0.70) is another way of explaining the electronic and structural behavior of B1 $\text{CrO}_x\text{N}_{1-x}$ films with an oxygen concentration x between 0.50 and 0.70. This is consistent with the shift of the main peaks and the VB edge (VBE) of the valence band structure toward higher BE with increasing x , as can be seen in Fig. 7. As can be seen the hybridized Cr 3d–N 2p peak lies predominantly on the Cr 3d–N 2p line for $x \leq 0.70$. Furthermore, the VBE, estimated from the XPS valence band curves, shifts from about -1.5 eV to 0.15 eV, with increasing x (see Fig. 8). In particular, the position of the VBE exhibits a sharp decrease above $x \sim 0.55$. The energy difference between the VBE and the Fermi energy level is related to the free electron

FIG. 7. XPS valence band spectra for the $\text{CrO}_x\text{N}_{1-x}$ films.

FIG. 8. Valence band edge versus x for the $\text{CrO}_x\text{N}_{1-x}$ films. The line is a guide for the eye only.

concentration and thus to the conductivity of the compound.²⁴ Therefore, the shift of the VBE toward lower values suggests an increasing resistance, which is consistent with previous studies on $\text{CrO}_x\text{N}_{1-x}$ coatings¹² and with the expected transition from conductive CrN (Ref. 12) to insulating Cr_2O_3 (Refs. 19 and 20). This result illustrates that it is possible to tune the electrical conductivity of chromium oxynitrides, by simply adjusting the nitrogen/oxygen atomic ratios.

An efficient and illustrative way to estimate the peak shifts independently from charge referencing is to plot the BE difference ΔBE between the peaks of interest versus x , as shown in Fig. 9. The ΔBE values between the O 1s and N 1s peaks do not undergo significant changes and are not reported here. As expected, the energy difference between the O 1s, the N 1s, and the Cr $2p_{3/2}$ peaks increases with

FIG. 9. Difference ΔBE of photoelectron binding energies between the Cr $2p_{3/2}$ and the Cr $2p_{1/2}$, O 1s, and N 1s peaks.

increasing the oxygen content, as shown by the BE evolution in Fig. 6. As mentioned above, nitrogen is only slightly affected by oxygen as a second neighbor, as suggested by the trend of the N 1s peak position in Fig. 6. Therefore the sharp increase of both the Cr $2p$ -N 1s and Cr $2p$ -O 1s energy difference is only caused by the Cr $2p_{3/2}$ shift, as a consequence of the charge transfer from chromium to the oxygen. An examination of the spin-orbit splitting of the Cr $2p$ peak provides another piece of information in the picture of the electronic structure of these coatings. The Cr $2p_{3/2}$ and the Cr $2p_{1/2}$ splitting are consequences of the spin-orbit coupling, which depends on the oxidation state and the chemical environment of the element. The measured ΔBE values between the Cr $2p_{3/2}$ and the Cr $2p_{1/2}$ peaks correspond to those found for CrN (~ 9.5 eV) for $x \leq 0.55$ (Ref. 34), ΔBE crosses the CrO value (~ 9.6 eV) for $x \approx 0.60$ (Refs. 6 and 34) and then increases to 10.0 eV for the Cr_2O_3 films, being close to the value of 9.9 eV observed in previous studies.³¹

To summarize the XPS results, the BE values for the Cr $2p_{3/2}$ and N 1s and the spin-orbit splitting energy between Cr $2p_{1/2}$ and Cr $2p_{3/2}$ for $x \leq 0.55$ align along those of CrN (Figs. 6 and 9, top graph), while the O 1s peak positions lie along the CrO line (Fig. 6). At higher oxygen contents with x between 0.55 and 0.69 the BE values of the Cr $2p_{3/2}$ increase gradually, crossing the CrO region (Fig. 6), as does the spin-orbit splitting energy (Fig. 9). For highest oxygen contents the BE finally reaches the value for Cr_2O_3 . The onset of a significant density of states at the valence band edge is found at values above the Fermi level (negative BE values) for nitride and monoxide films which is in accordance with their electrical conductivity^{18,19} (not measured in this work) and their crystal structure (B1, Figs. 2 and 3). For high oxygen contents ($x > 0.69$) the density of states at the Fermi level decreases dramatically, an expected finding for a material in the corundum structure, as are these films for oxygen contents at $x \geq 0.97$. In other words, the XPS results, being consistent with the structural data, indicate that the material behaves electronically like a nitride for $x \leq 0.55$, as a monoxide for intermediate x , and as Cr_2O_3 for x close to 1.00.

IV. CONCLUSIONS

The present study shows that the crystallographic and electronic properties of $\text{CrO}_x\text{N}_{1-x}$ films can be tuned in a wide range by varying the oxygen concentration x . The samples with $x \leq 0.70$ crystallize in the B1 structure and samples adopt the corundum structure for higher x . The gradual decrease of the stress-free lattice parameter of the samples with the B1 structure with increasing x indicates that oxygen atoms substitute for nitrogen atoms in the B1 $\text{CrO}_x\text{N}_{1-x}$. This incorporation goes in parallel with an enhanced (002) preferred orientation with increasing x . The electronic properties, in terms of the photoelectron binding energies (BE) of the samples and the valence band (VB) electronic structure, indicate that the B1 $\text{CrO}_x\text{N}_{1-x}$ acquire progressively the properties of chromium monoxide for x between 0.70 and 0.97 and change to the Cr_2O_3 corundum structure at oxygen contents x close to unity. The introduction of oxygen results

in a charge transfer from Cr to O, inferred by the increase of the Cr 2p_{3/2} BE. A shift of the VB toward higher BE suggests a change of conductive properties of the films with increasing oxygen content. This transition correlates with a change in the electronic properties from a conductive to an insulating material, while the B1 CrO_xN_{1-x} structure is still maintained for values of x at least as high as 0.70.

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