



HAL
open science

Structure and optical properties of CrO_xN_y films with composition modulation

Yanyan Yuan, Bingye Zhang, Jian Sun, Philippe Jonnard, Karine Le Guen, Yuchun Tu, Chao Yan, Rui Lan

► **To cite this version:**

Yanyan Yuan, Bingye Zhang, Jian Sun, Philippe Jonnard, Karine Le Guen, et al.. Structure and optical properties of CrO_xN_y films with composition modulation. *Surface Engineering*, 2020, 36 (4), pp.411-417. 10.1080/02670844.2019.1656356 . hal-02616495

HAL Id: hal-02616495

<https://hal.science/hal-02616495v1>

Submitted on 24 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Structure and optical properties of CrO_xN_y films with composition modulation

Yanyan Yuan^{a*}, Bingye Zhang^a, Jian sun^a, Philippe Jonnard^b, Karine Le Guen^b, Yuchun Tu^c, Chao Yan^{a*}, Rui Lan^a

^a*National Demonstration Center for Experimental Materials Science and Engineering Education (Jiangsu University of Science and Technology), Zhenjiang 212003, P. R. China;*

^b*Sorbonne Université, Faculté des Sciences et Ingénierie, UMR CNRS, Laboratoire de Chimie Physique-Matière et Rayonnement, 4 place Jussieu, F-75252 Paris cedex 05, France*

^c*Shanghai Institute of laser plasma, No.1129, Chengjiashan road, Jiading district, Shanghai, 201800, P.R.China*

*corresponding author: yuan.yanyan@just.edu.cn; chaoyan@just.edu.cn

Abstract

The composition and structure properties of the CrO_xN_y films deposited by RF reactive magnetron sputtering were investigated and correlated with their optical properties. Two kinds of targets Cr₂O₃ and CrN compounds with variation of N₂ and O₂ gas flow were used to prepare two series of samples. The phase structure, chemical composition and optical properties of CrO_xN_y films were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and ultraviolet-visible-near-infrared spectrophotometer, respectively. The films mainly consist of Cr₂N and CrO₃ phases.

The Cr/ON ratio derived by XPS varies with the variation of nitrogen with Cr₂O₃ target.

But only lower nitrogen content is detected with variation of oxygen using CrN target.

The CrO_xN_y films with higher nitrogen content possess high absorbance around at 35% in the visible light range no matter the target.

Keywords: chromium oxynitride; optical properties; composition modulation; XPS

1. Introduction

Transition metal nitrides and oxides have received considerable interests due to their versatile properties. They are frequently applied in optical devices, such as solar cell electron transport materials^[1,2]. On the other hand, transition metal nitrides such as CrN, TiN, ZrN exhibit excellent physical properties like relatively high hardness, high melting point and good chemical stability. Furthermore, for some of them their performance can be improved by ternary, quaternary and multicomponent thin films preparation through addition of other refractory materials^[3,4,5,6].

In addition, a combination of transitional metal nitrides and oxides as oxynitrides promises the possibility to tune the structural, optical and electrical properties in a wide range as desired for various applications, like hard coatings, decorative coatings as well as solar devices. See for example, some works on these TiO_xN_y^[7,8], ZrO_xN_y^[9,10,11], TaO_xN_y^[12] films. However chromium nitrides and oxides with potential properties such as high chemical stability, wear and corrosion resistance as well as optical properties have received great attention.

The chromium oxynitride films, whose properties could be tuned between their

corresponding oxides and nitrides, can be formed through the addition of a small amount of oxygen into chromium nitrides or nitrogen into the oxides. They possess many potential interesting applications due to their versatile properties, like electrical, optical, mechanical and tribological properties achieved by tuning N/O composition.

Chromium oxynitride can be considered as a mixture of CrN and Cr₂O₃ rather than a single phase chromium oxynitride. Therefore, it has the hardness of Cr₂O₃ and the toughness of CrN materials. Otherwise, CrN_x shows a metallic-like ($\rho \approx 6.4 \times 10^{-4} \Omega \text{cm}$, $x \approx 0.93$) or semiconducting behavior ($\rho > 1 \times 10^{-2} \Omega \text{cm}$, $x \approx 1.06$) depending on its stoichiometry, while CrO_x is an insulator ($E_g \approx 4 \text{eV}$, $\rho_{\text{Cr}_2\text{O}_3} \gg 1 \Omega \text{cm}$). The CrO_xN_y thin films combining both materials show the possibility to tune the energy band gap. Recently it has been reported by Zheng et al. that the chromium oxides show potential application in planar perovskite solar cell as electron transport material for enhancing the stability of solar cells ^[1]. It has been reported that chromium oxynitride (CrO_xN_y) films can often be prepared by using reactive magnetron sputtering ^[13] and pulsed laser deposition techniques ^[14]. Suzuki reported that the oxygen content in the Cr(N,O) film prepared by pulse laser deposition can significantly improve its hardness up to be 30 GPa ^[15]. The chromium oxynitride films have different colors with variation of thickness and composition as decorative coatings ^[16]. Wierzchon et al. reported that the CrO_xN_y films show higher corrosion resistance as well as better adhesion and uniform structure than that of Cr₂O₃ films ^[17]. K Sushant et al. reported that the transmittance and band gap values of CrON films increase with the increase of oxygen partial pressure ^[18].

This paper study the CrO_xN_y thin films prepared by RF magnetron sputtering with Cr₂O₃ and CrN targets using oxygen and nitrogen as reaction gases. The structure, surface

composition and optical properties of the CrO_xN_y thin films were investigated by grazing incidence X-ray diffraction (GIXRD), x-ray photoelectron spectroscopy (XPS) and ultraviolet-visible-near-infrared spectrophotometer, respectively. The main goal of the present paper is to develop a method to slightly control the N/O ratio in the films.

2. Experimental details

The chromium oxynitride thin films were deposited on Si (111) substrates and ITO-glass substrates by using radio frequency (RF) reactive magnetron sputtering technology (JCP-500M3 Beijing Technol. Co. LTD., China) with Cr_2O_3 (99.5%) and CrN (99.5%) targets. The base pressure was around at 6.0×10^{-4} Pa before deposition. The working gas was argon (99.999%) with reactive gases oxygen and nitrogen keeping at a constant working pressure of 1.0 Pa. The target–substrate distance was about 100 mm. When the Cr_2O_3 or CrN was used as target, nitrogen or oxygen flow rate varied with the value of 5, 8, 10 sccm and 3, 5, 8, 10 sccm respectively, but kept the total constant flow rate of 25.0 sccm. The power applied on all the targets was set as 100 W. All samples were deposited at room temperature. Five minutes pre-sputtering was performed on the targets before depositing all samples.

The phase structures of the films were measured via grazing incidence X-ray diffraction (GIXRD) using D8 Advance A25 with Cu $K\alpha$ radiation ($\lambda = 0.1542$ nm) at 40 kV and 10 mA. The grazing incidence angle was set as 4° .

The surface chemical composition and chemical bonding states of the CrO_xN_y thin films were investigated through XPS using Escalab 250Xi system (Thermo Scientific) equipped with an Al $K\alpha$ source (1486.6eV). The surface chemical composition was quantified using

Avantage software. The absorbance of the CrO_xN_y thin films was observed using an ultraviolet-visible-near-infrared spectrophotometer (UV-3600, Shimadzu).

3. Results and discussion

3.1 X-ray photoelectron spectroscopy

Figure 1 shows the XPS spectra of the Cr2p, O1s and N1s core levels of the CrO_xN_y thin films prepared by using Cr_2O_3 target with variation of nitrogen flow rate. The peak position of Cr 2p spectra slightly shift toward higher binding energies when the nitrogen flow rate exceeds 8sccm, meanwhile the peak intensity increases. Regarding the O 1s spectra shown in Figure 1 (b) the peak position shifts toward the lower binding energy with the increase of nitrogen flow rate. However there is no significant peak position shift with an exception of peak intensity change. It is known that the peak position shift and peak intensity could reflect the change in chemical bonds and element content, respectively. Therefore for the N1s spectra, the N content increases when the nitrogen flow rate is 5 and 8 sccm but decreases again with 10sccm of nitrogen. Otherwise peak shift and peak intensity of the Cr2p and O1s spectra indicates the variation of the chemical bond state and atomic content in the samples surface. The atomic ratios in the samples will be discussed in the following part.

Figure 2 shows the XPS spectra of the Cr2p, O1s and N1s core level of the CrO_xN_y thin films prepared by using CrN target with variation of the oxygen flow rate. Regarding the Cr2p spectra, shown in Figure 2 (a) the peak position shift significantly toward high binding energies when the oxygen flow rate exceeds 8 sccm. According to the literature ^[19], the shift

of the Cr 2p spectra is assigned to the formation of Cr-O and/or Cr-N bonds. In view of the O1s spectra shown in Figure 2(b) the peak position shifts slightly toward lower binding energy with variation of the oxygen flow rate. For the N1s spectra, shown in Figure 2(c), no strong N signal was detected with oxygen introduction. That is to say there is less N content at the sample surface when oxygen was introduced into the chamber even we use the CrN target. The reason is due to the oxidation of the samples when they are stored in the air, leading to a part of O content incorporated after deposition. However the oxidation of the CrN target surface during deposition should be also responsible for the lower N content in the films.

Figures 3 and 4 present the fitted spectra of the samples prepared using Cr₂O₃ and CrN targets, respectively to further understand the change of the chemical bond state in the samples. All the fitted spectra have been done by using Gaussian-Lorentzian peaks and Shirley background. Figure 3(a) shows the Cr2p fitting spectra of four samples prepared with Cr₂O₃ target. The Cr2p_{3/2} peak of the sample prepared with nitrogen flow rate exceed 5 sccm is fitted with three peaks. It means that three kinds of Cr chemical bond states exist in the sample. But for the sample prepared without nitrogen the Cr2p_{3/2} peaks is fitted with two peaks components. Compared with the Cr2p_{3/2} core level binding energy value of 574.3 eV in the pure Cr, the Cr2p_{3/2} peaks in the films shift toward high binding energy by 2.3-3.2 eV. Table1 concludes binding energy of the fitted peaks of the Cr 2p and O 1s spectra as well as corresponding chemical bond. The component around at 579 eV is ascribed to the Cr-O bond from CrO₃ compound. The major component at around 577 eV is attributed to Cr-O-N bond. According to literature [20], the component at 576.0 eV is attributed to Cr-O bond from Cr₂O₃. In Figure 3 (b), for the samples prepared without nitrogen, the fitting of the O1s peak clearly

shows the existence of three peaks components. The component at 532.5eV corresponds to N-O bond and the components located at around 531.6 and 530.7eV correspond to O-H and Cr-O bond, respectively. The existence of O-H bond is due to absorption water on the sample surface. The O1s spectra show a broad feature with increase of nitrogen flow rate indicating the high oxygen content. Note that the samples prepared with nitrogen flow rate of 10 sccm and 5 sccm, the O1s peak is fitted with four peaks components. It indicates the change of O chemical bond state in the sample.

The N1s fitting spectra are shown in Figure 3(c). The high nitrogen content in the sample prepared with 10 sccm of nitrogen is confirmed by the broad feature. Meanwhile N1s peak is fitted with four peaks components. The component at 399.9eV corresponds to the N-O bond. The other components at 398.0, 396.8 and 398.8eV probably correspond to the Cr-N from Cr₂N and CrN_x, respectively.

Figure 4 shows fitted XPS spectra for the CrO_xN_y films prepared using CrN target. The peak intensity of the shoulder located at high binding energy (579.6eV) increases with increase of oxygen. The components located at more than 578eV correspond to the Cr-O bond in the CrO₃ compound. The components at around 577.5eV correspond to the Cr-N bond in the Cr₂N compound. The component at 576 eV is attributed to Cr-O bond from Cr₂O₃[20]. The fitted O1s spectra, shown in Figure 4 (b) conclude four components for all samples. The component located around at 532-532.7 eV belongs to N-O bond and the component located at 530.7 eV belongs to Cr-O from Cr₂O₃ compound.

Table 2 listed the atomic ratio of each element in chromium oxynitride thin films derived

from XPS spectra using Avantage software. It is shown that the surface chemical composition of the CrO_xN_y films prepared using Cr_2O_3 target show a variation of Cr/NO ratio dependence on the reactive gases. The Cr/O ratio is about 1:4 when the sample is prepared using Cr_2O_3 target with only argon, which is quite different from the Cr/O ratio of the target. It means that the oxidation occurred on the surface of the samples when they are stored in air. However, the N content in the films decreases with increase of nitrogen flow rate. The Cr/NO ratio slightly increase with increase of nitrogen flow rate. There is no doubt that N atoms are introduced into the films and the N content varies depending on the variation of the nitrogen flow rate even the O content is always higher than N content. The main reason for higher O/Cr ratio than N/Cr is due to the large difference in electronegativity between Cr and O which makes Cr-O bonds easier to be formed.

Regarding the samples prepared using CrN target, it can be seen that all the samples have lower N content even without oxygen introduction. The Cr/N ratio in the target is around 2:1 before sputtering measured by EDX. When the samples are prepared using CrN target without oxygen, the N content is quite low and much less than the O content. The Cr/NO ratio in the films is about 1:3 and is very different from the target value. Moreover, the N content in the films decreases a lot with the introduction of oxygen compared with the N content without oxygen. The main reason for the low N content is due to the oxidation as well as the loss of nitrogen during sputtering process.

3.2 Grazing incidence X-ray diffraction (GIXRD)

Figure 5 shows the phase structures of the chromium oxynitride thin films. In addition,

the XRD pattern of the Si substrate is also shown here for comparison. There is no diffraction peak of the Si substrate in the measurement range. The samples prepared using Cr₂O₃ target with N₂ reactive gas show an intense peak located at around $2\theta=57.5^\circ$ which corresponds to CrO₃(003). Otherwise, a shoulder located at $2\theta=56^\circ$ along the strong peak appeared, which probably corresponds to Cr₂N (112). A weak peak located at $2\theta=77.5^\circ$ probably corresponds to CrO₃ (402). The results are in agreement with the XPS-derived Cr/O ratio. When the sample prepared using CrN target with 10 sccm of oxygen flow rate, the peak position is same as these prepared using Cr₂O₃ target. However, the sample deposited using Cr₂O₃ target with 5 sccm of oxygen flow rate shows an intense peak located at $2\theta=56^\circ$, which corresponds to Cr₂N (112). It is not in agreement with the XPS-derived atomic ratio. But one thing should be noted that the XPS-derived atomic ratio is from the sample surface. However the XRD pattern shows the whole sample information.

3.3 Optical properties

To observe the effect of composition on the optical properties of the samples, the absorbance spectra was measured and shown in Figure 6. Figure 6 (a) show the absorbance spectrum of the chromium oxynitride thin films prepared with Cr₂O₃ target with variation of nitrogen. The results present that the absorbance increases slightly with decrease of the nitrogen flow rate in the range of 300-800 nm. The absorption edge of the sample prepared with 5 sccm of nitrogen is located at around 450 nm and the absorption edge shifts toward the short wavelengths direction as the nitrogen flow rate increases. Figure 6 (b) shows the absorbance spectra of the chromium oxynitride thin films deposited using CrN target with

variation of oxygen. The absorption edge is located at about 400 nm and the absorbance is around 0.2% in the visible range for all samples. There is no obvious shift of the absorption edge with increase of the oxygen flow rate.

4 . Conclusions

We study the effects of the reactive atmosphere on the crystal structure, chemical state and composition as well as optical properties of the CrO_xN_y films. The XRD results demonstrated the coexistence of Cr_2N and CrO_3 compounds of all samples. The films prepared using Cr_2O_3 target possesses the preferred CrO_3 (003). However, the preferred orientation of the film prepared using CrN target is converted from Cr_2N (112) to CrO_3 (003) as the oxygen flow rate increases. XPS results indicate that the composition of the CrO_xN_y films can be easily modulated by using the Cr_2O_3 target than CrN target. Absorbance of the CrO_xN_y films prepared with Cr_2O_3 target shows no significant change only the sample with high N content possess high absorbance around 35% in the visible light range.

Disclosure statement

No potential conflict of interest was reported by the authors.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51702133) and by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

- [1] Shizhao Zheng, Wenlang Li, Tongtong Su, et al. Metal Oxide CrO_x as a Promising Bilayer Electron Transport Material for Enhancing the Performance Stability of Planar Perovskite Solar Cells, *Sol. RRL*, 2018, 1700245(6pages)
- [2] N. Martin, A. Besnard, F. Sthal, et al. The contribution of grain boundary barriers to the electrical conductivity of titanium oxide thin films, *Appl. Phys. Lett.* 2008, (93): 064102.
- [3] Hongbo Ju, Junhua Xu. Influence of vanadium incorporation on the microstructure, mechanical and tribological properties of Nb–V–Si–N films deposited by reactive magnetron sputtering, *Materials Characterization*, 2015, (107):411–418.
- [4] Hongbo Ju, Junhua Xu, Microstructure, oxidation resistance, mechanical and tribological properties of Ti–Y–N films by reactive magnetron sputtering, *Surface & Coatings Technology*, 2015 (283): 311–317.
- [5] Junhua Xu, Hongbo Ju, Lihua Yu. Influence of silicon content on the microstructure, mechanical and tribological properties of magnetron sputtered Ti–Mo–Si–N films, *Vacuum* 2014, (110):47-53.
- [6] Lihua Yu, Jian Chen, Hongbo Ju, et al. Influence of Al content on microstructure, mechanical and tribological properties of Ti–W–Al–N composite films, *Vacuum*, 2017, (137):31-37.
- [7] E. Alves, A.R. Ramos, N.P. Barradas, F. Vaz, P. Cerqueira, L.Rebouta, U. Kreissig, Ion beam studies of TiN_xO_y thin films deposited by reactive magnetron Sputtering, *Surf. Coat. Technol.* 2004, (372-376): 180–181.
- [8] R.J. Koerner, L.A. Butterworth, I.V. Mayer, R. Dasbach, H.J. Buucher, Bacterial adhesion to titanium-oxy-nitride (TiNOX) coatings with different resistivities: a novel approach for the development of biomaterials, *Biomaterials*, 2002 (23):2835-2840
- [9] Yanyan Yuan, Rui Lan, Chao Yan and Rui Liu, Zirconium oxynitride films: Modulation of component as a function of the preparation parameters, *Modern Physics Letters B*, 2018, (32): 34-36.
- [10] C.I. da Silva Oliveira, D. Martinez-Martinez, L. Cunha, M.S. Rodrigues, J. Borges, C. Lopes, E. Alves, N.P. Barradas, M. Apreutesei, Zr–O–N coatings for decorative purposes: Study of the system stability by exploration of the deposition parameter space, *Surface & Coatings Technology*, 2018 (343):30–37.
- [11] G.I. Cubillos, M.E. Mendoza, J.E. Alfonso, G. Blanco, M. Bethencourt, Chemical composition and microstructure of zirconium oxynitride thin layers from the surface to the substrate-coating interface, *Materials Characterization* 2017, (131): 450–458.

- [12] C.K. Chung , T.S. Chen, N.W. Chang, Effect of reactive gases flow ratios on the microstructure and electrical resistivity of Ta–N–O thin films by reactive co-sputtering, *Thin Solid Films*, 2011, (519): 5099–5102.
- [13] Sushant K. Rawal, Amit Kumar Chawla, Vipin Chawla, R. Jayaganthan, Ramesh Chandra, Structural and optical investigation of sputter deposited hydrophobic chromium oxynitride films, *Thin Solid Films*, 2011, (519):7686–7693.
- [14] Tsuneo Suzuki, Jun Inoue, Hajime Saito, Makoto Hirai, Hisayuki Suematsu, Weihua Jiang, Kiyoshi Yatsui, Influence of oxygen content on structure and hardness of Cr–N–O thin films prepared by pulsed laser deposition, *Thin Solid Films* ,2006, (515): 2161–2166.
- [15] K. Suzuki, T. Endo, T. Fukushima, A. Sato, T. Suzuki, T. Nakayama, H. Suematsu, K. Niihara, Controlling oxygen content by varying oxygen partial pressure in chromium oxynitride thin films prepared by pulsed laser deposition, *Mater. Trans.* 2013, (54):1140–1144.
- [16] R. Mientus, R. Grotchel, K. Ellmer, Optical and electronic properties of CrO_xN_y films, deposited by reactive DC magnetron sputtering in Ar/N₂/O₂(N₂O) atmospheres, *Surf. Coat. Technol.* 2005, (200): 341-345.
- [17] T. Wierzchon, I. Ulbin-Pokorska, K. Sikorski, Corrosion resistance of chromium nitride and oxynitride layers produced under glow discharge conditions, *Surf. Coat. Technol.* 130 (2000) 274–279.
- [18] Sushant K. Rawal, Amit Kumar Chawla, Vipin Chawla, R. Jayaganthan, Ramesh Chandra , Structural and optical investigation of sputter deposited hydrophobic chromium oxynitride films , *Thin Solid Films*, 2011, (519) 7686–7693
- [19] I.Milosev, H.H.Strehblow, B.Navinsek, Comparison of TiN, ZrN and CrN hard nitride coatings: Electro chemical and thermaloxidation, *Thin Solid Films*, 1997, (303) 246–254.
- [20] Mohammad Sharear Kabir, Paul Munroe, Zhifeng Zhou, Zonghan Xie Structure and mechanical properties of graded Cr/CrN/CrTiN coatings synthesized by close field unbalanced magnetron sputtering, *Surface & Coatings Technology* 2017, (309): 779–789.

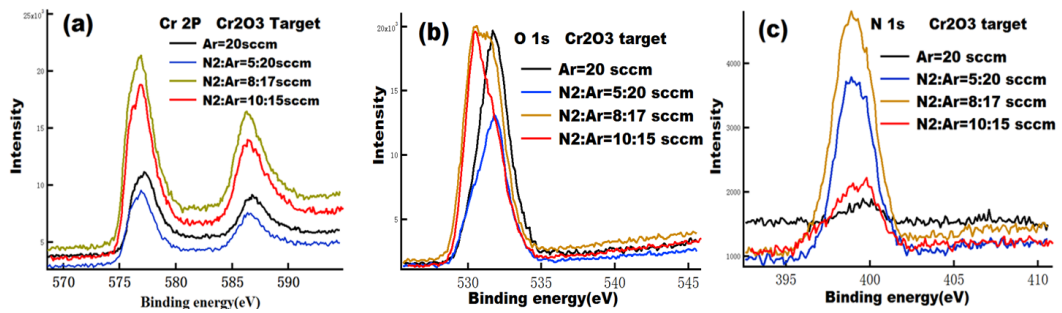


Figure 1. XPS spectra recorded from chromium oxynitride thin films prepared by using Cr_2O_3 target with variation of nitrogen: (a) Cr 2p; (b) O 1s; (c) N 1s.

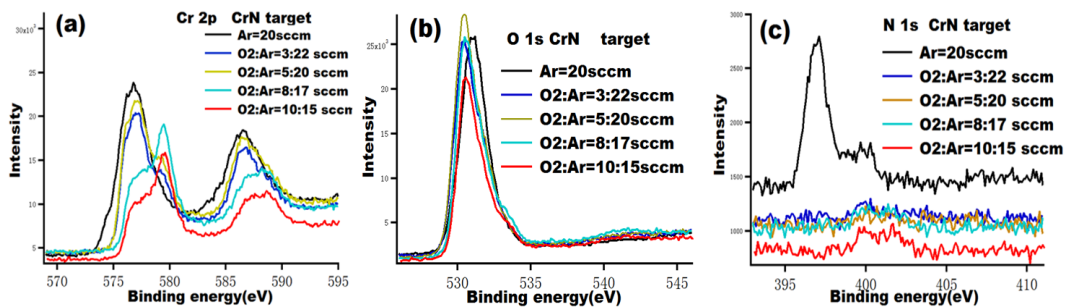


Figure 2 XPS spectra recorded from the chromium oxynitride thin films prepared using CrN target with variation of oxygen flow rate: (a) Cr 2p; (b) O 1s; (c) N 1s.

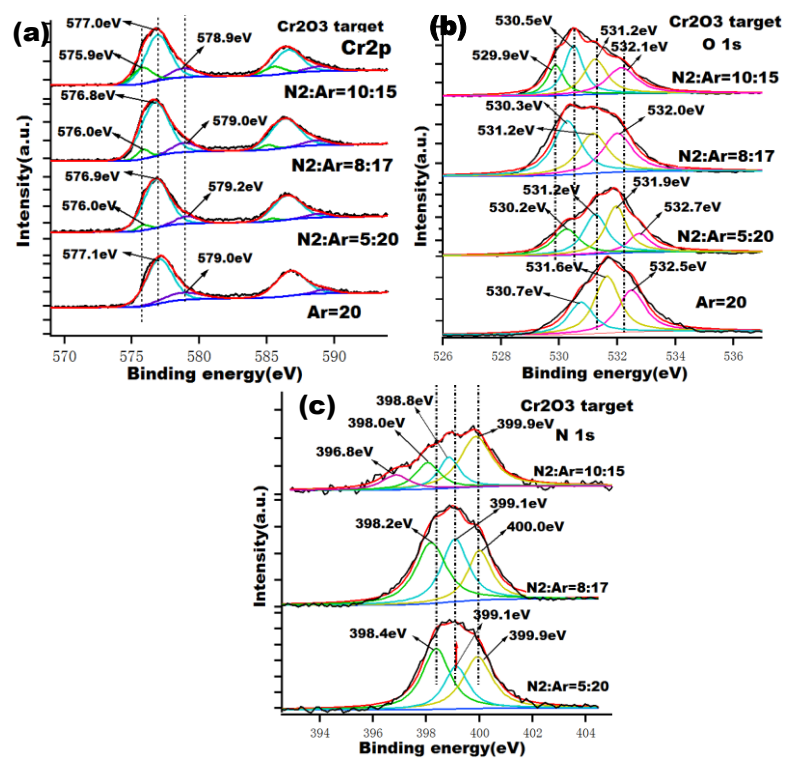


Figure 3. Fitted XPS spectra for the chromium oxynitride thin films prepared using Cr_2O_3 target with variation of nitrogen flow rate: (a) Cr 2p, (b) O 1s and (c) N 1s.

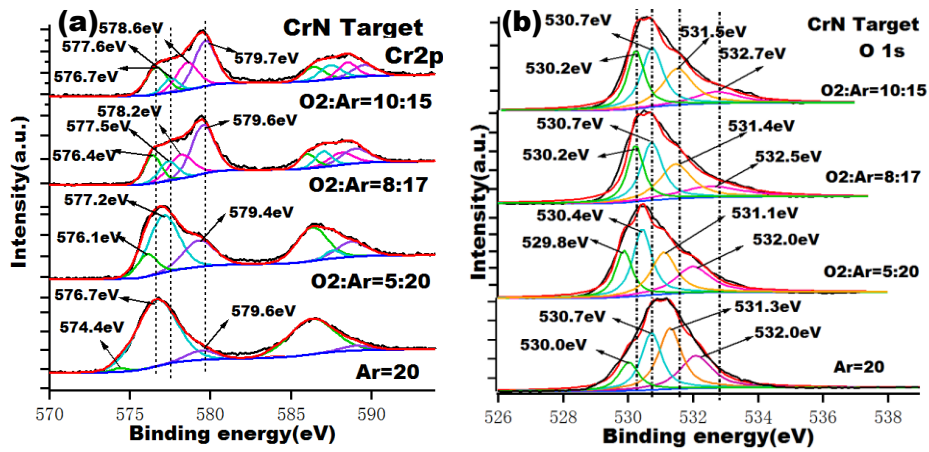


Figure 4. Fitted XPS spectra for the chromium oxynitride thin films prepared using CrN target with variation of oxygen flow rate: (a) Cr 2p, (b) O 1s.

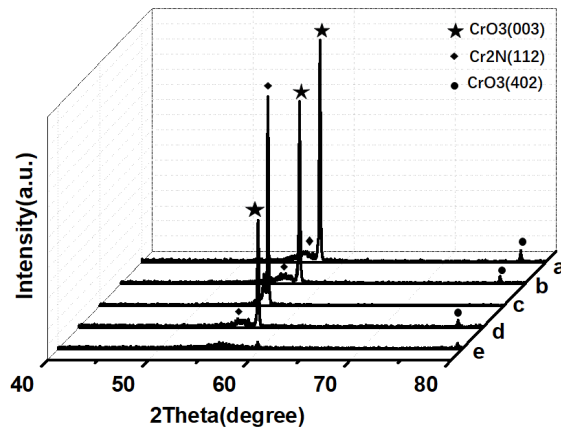


Figure 5. GIXRD patterns of the CrO_xN_y films prepared using Cr_2O_3 (a: N_2 : Ar =8:17sccm; b: N_2 : Ar =10:15 sccm) and CrN targets (c: O_2 : Ar =5:20sccm; d: O_2 : Ar =10 : 15 sccm), e: Si substrate.

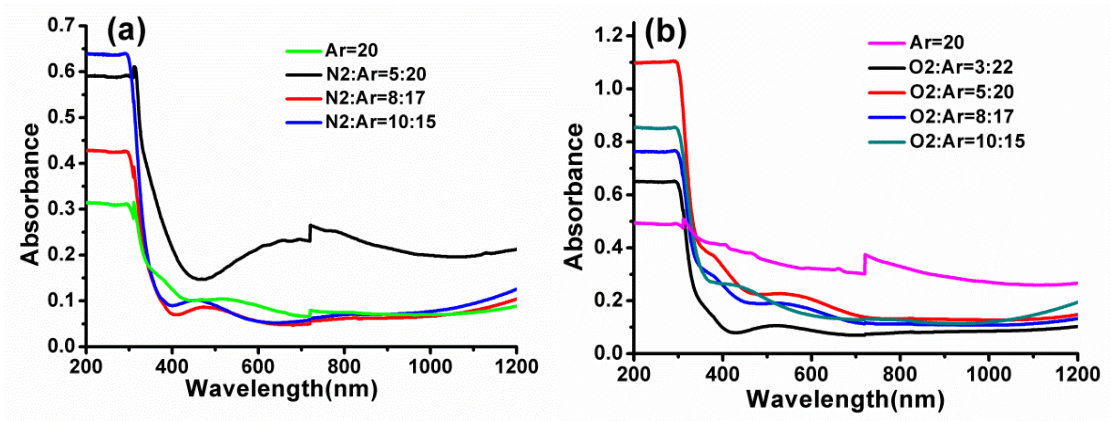


Figure 6. Absorbance spectra of chromium oxynitride films: (a) Cr_2O_3 target, (b) CrN target.

Table 1 Binding energy and chemical bond of the fitted peak components of the Cr2p and O1s spectra of the samples. BE: binding energy (eV); CB: chemical bond (corresponded compounds are in the parentheses). The samples prepared using Cr₂O₃ target with nitrogen flow rate of 0, 5, 8 and 10 sccm are labeled as S10, S11, S12 and S13, respectively. The samples prepared using CrN target with oxygen flow rate of 0, 5, 8 and 10 are labeled as S20, S21, S22 and S23 respectively.

Samples	Cr 2p				O 1s			
		BE(eV)	577.1	579.0	530.7	531.6	532.5	
S10	CB	Cr-O-N	Cr-O(CrO ₃)	Cr-O (CrO ₃)	O-H	O-N		
	BE(eV)	576.0	576.9	579.2	530.2	531.2	531.9	532.7
S11	CB	Cr-O (Cr ₂ O ₃)	Cr-N (Cr ₂ N)	Cr-O (CrO ₃)	Cr-O (CrO ₃)	O-H	O-N	
	BE(eV)	576.0	576.8	579.0	530.3	531.2	532	
S12	CB	Cr-O (Cr ₂ O ₃)	Cr-N (Cr ₂ N)	Cr-O (CrO ₃)	Cr-O (CrO ₃)	O-H	O-N	
	BE(eV)	575.9	577.0	578.9	529.9	530.5	531.2	532.1
S13	CB	Cr-O (Cr ₂ O ₃)	Cr-O-N	Cr-O (CrO ₃)	Cr-O (Cr ₂ O ₃)	Cr-O (CrO ₃)	O-H	O-N
	BE(eV)	574.4	576.7	579.6	530.0 530.7	531.3	532.0	
S20	CB	Cr-Cr	Cr-N (Cr ₂ N)	Cr-O (CrO ₃)	Cr-O (Cr ₂ O ₃)	O-H	O-N	
	BE(eV)	576.1	577.2	579.4	529.8 530.4	531.1	532.5	
S21	CB	Cr-O (Cr ₂ O ₃)	Cr-N (Cr ₂ N)	Cr-O (CrO ₃)	Cr-O (Cr ₂ O ₃)	O-H	O-N	
	BE(eV)	576.4	577.5	578.2 579.6	530.2 530.7	531.4	532.5	
S22	CB	Cr-O (Cr ₂ O ₃)	Cr-O-N	Cr-O (CrO ₃)	Cr-O (Cr ₂ O ₃)	O-H	O-N	
	BE(eV)	576.7	577.6	578.6 579.7	530.2 530.7	531.5	532.7	
S23	CB	Cr-O (Cr ₂ O ₃)	Cr-O-N	Cr-O (CrO ₃)	Cr-O (Cr ₂ O ₃)	O-H	O-N	

Table.2 Atomic ratio of the chromium oxynitride thin films derived from XPS spectra.

Target	Atmosphere	Atomic ratio (at.%)		
		Cr	O	N
Cr ₂ O ₃	Ar=20sccm	19.5	80.5	--
	N ₂ :Ar=5:20sccm	14.1	59.7	26.2
	N ₂ :Ar=8:17sccm	20.4	58.9	20.7
	N ₂ :Ar=10:15sccm	23.5	66.1	10.4
CrN	Ar=20sccm	29.0	64.0	7.0
	O ₂ :Ar=3:22sccm	24.9	72.7	2.4
	O ₂ :Ar=5:20sccm	25.7	71.8	2.5
	O ₂ :Ar=8:17sccm	21.8	75.1	3.1
	O ₂ :Ar=10:15sccm	22.3	74.2	3.5