EFFECT OF N₂ PARTIAL PRESSURE ON THE GROWTH OF CHROMIUM NITRIDE COATINGS.

F. Capotondi, L. Rettighieri, A. Ballestrazzi, L. Calabri, P. Ferrarini, C. Menozzi, S. Valeri

Chromium nitride films has been prepared by reactive magnetron sputtering using a mixture of Ar and N₂ gas. Keeping constant the total pressure during the film deposition the ratio of N₂ to Ar has been varied from 0.3 to 5.0 to promote the growth of CrN films with different microstructure. The structural chemical characterization of grown films were performed by means of x-ray diffraction and scanning electron microscopy, auger electron spectroscopy and x-ray photoemission spectroscopy. Even if no clear correlation between material hardness and coating microstructure was observed with nanoindentation, the tribological characterization of the films, evidenced a strong dependence of the wear rate of the material by the process conditions. In particular we observed an improved wear resistance for coatings with a compressive residual stress.

KEYWORDS: reactive magnetron sputtering, chromium nitride, wear, XRD, XPS, AES

INTRODUCTION

Nitride coatings are used in a broad variety of technological applications due to their interesting combination of physical and chemical properties [1-3]. These coatings are generally prepared by physical vapour deposition techniques (ion plating, sputtering, arc evaporation) allowing the formation of dense adhesive films at low deposition temperatures. Titanium nitride (TiN) is the coating most extensively used in industry to improve the performance of different cutting tools, however to withstand aggressive environments either a third element (commonly Al) or an interlayer (sputtered Ti or electrochemical Ni) must be added [4,5]. In recent years chromium nitride (CrN) films have been widely used for industrial applications, becoming important technological ceramic material due to the excellent physical and mechanical properties such us high surface hardness, toughness and corrosion resistance

F. Capotondi, L. Calabri, C. Menozzi
CNR-INFM-National Research Centre on nanoStructures and bioSystems at Surfaces (S3.)
P. Ferrarini
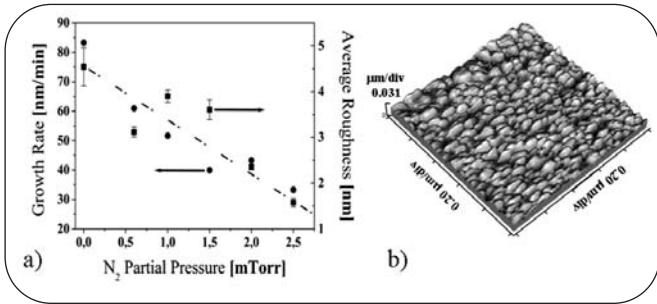Dipartimento di Fisica, Modena, Italy
A. Ballestrazzi
STAR s.r.l., Modena, Italy
L. Rettighieri
CNR-INFM-National Research Centre on nanoStructures and bioSystems at Surfaces (S3.) - STAR s.r.l., Modena, Italy
S. Valeri
CNR-INFM-National Research Centre on nanoStructures and bioSystems at Surfaces (S3.) - Dipartimento di Fisica, Modena, Italy

[6,7]. The main fields of application are: cutting and forming tools, bearings, machine parts, dies and moulds. In contrast with TiN coatings, the good performance of CrN films in aggressive environments is due to the formation of a passivating oxide layer which preserves the film from further oxidation [8]. Therefore CrN coatings are expected to keep their excellent wear resistance even under severe tribological conditions, such as high temperature, working speed and applied load. Among the different deposition techniques, reactive magnetron sputtering produces nitride coating with the best mechanical properties [9]. This is mainly related to the fine control of the process parameters (i.e. partial pressure, substrate temperature and applied bias) which affect the microstructural evolution of the coating. Depending on the nitrogen flow rate, four different phases of such ceramic material can be identified: (i) at extremely low N₂ flow, nitrogen is incorporate as a dopant inside the Cr crystal structure, (ii) at higher flow the film grows as a mixture of separate phases Cr+N+Cr₂N, (iii) increasing further the amount of nitrogen a mixture of Cr₂N +CrN is usually observed, (iv) finally at high N₂ flow the coating presents a single phase CrN [10].

In this report we study how the mechanical properties of the CrN coating are influenced by the micro-structural evolution related with the different N₂ partial pressure used during the growth process. We found that at the same homologous deposition temperature T_s/T_m (where T_s and T_m are respectively the substrate temperature and the melting point of the coating material) the microstructure evolves from a fine grain structure without voids corresponding to zone III in the Thornton's structural-zone-model [11] to a fully dense fibrous structure, having almost equiaxed grains and a structure equivalent to

a) Growth rate and AFM average roughness of CrN coatings as a function of the N₂ partial pressure used during the growth process. b) AFM image (1 x 1 µm) of the surface topography of the sample growth with a N₂ partial pressure of 2.5 mTorr: the surface is characterized by small grains of an average size of 50 nm.
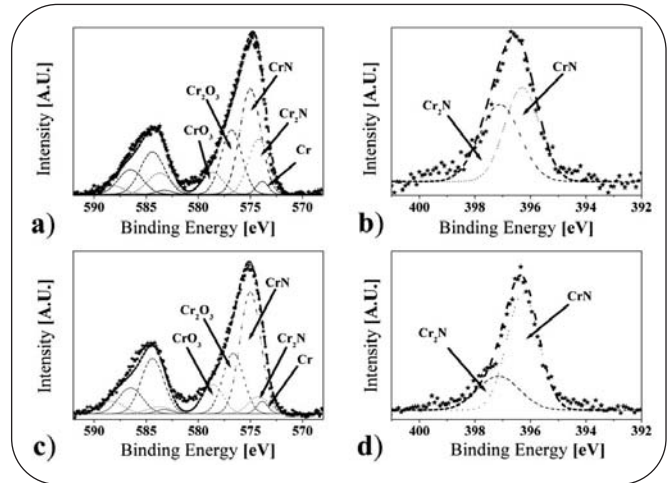
a) Tasso di crescita e rugosità dei film depositati in funzione della pressione parziale di N₂ utilizzata durante il processo. b) Immagine AFM (1 x 1 µm) della topografia del campione cresciuto a una pressione parziale di N₂ di 2.5 mTorr: la rugosità della superficie è caratterizzata dalla presenza di grani della dimensione di 50 nm.

zone II. At the same time increasing the N_2 flow, the coating internal stress changes from tensile to compressive. As a consequence the wear rate of material is strongly reduced.

EXPERIMENTAL DETAILS

Chromium nitride thin films were deposited by reactive DC magnetron sputtering on a (100) Si substrate, using a 3 inch Cr target (purity 99.95%) in an Ar+N_2 (both of 99.999% purity) atmosphere. Before the deposition, the base pressure in the chamber was less than $3x10^{-6}$ Torr. During the process deposition the total pressure, given by the sum of Ar and N_2 partial pressure was 3.0 mTorr. We changed the ratio of the N_2 and Ar gases from 0.3 (N_2 partial pressure = 0.7 mTorr) to 5.0 (N_2 partial pressure = 2.5 mTorr) keeping all other deposition parameters constant. Since the ion bombardment favour the densification of grown film to increase such parameter the substrate to target distance was setted to 50 mm, in such way the sputtered atoms are not thermalized by collisions with the sputtering gas mixture [12]. The substrate temperature was kept to 300°C, corresponding for CrN to a homologous deposition temperature T_s/T_m of about 0.3. The target current of the magnetron source was fixed at 0.4 A, with a voltage variation from 320 V to 390 V by increasing the N_2 partial pressure from 0.7 mTorr to 2.5 mTorr. This voltage changes is related to the higher discharge impedance between the electrodes as a consequence of the lower ionization probability of N_2 with respect to Ar. The deposition time was kept constant to 30 min. for all deposition so, the total thickness of coatings ranges from 1 µm to 1.8 µm, due to the different growth rate (see Fig. 1 a)).
The chemical analysis of the coating, was performed by X-ray Photoemission Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) in ultra high vacuum chamber (less than $8x10^{-9}$ Torr). XPS measurements were performed by a Leybold-Heraeus electron hemispherical analyser equipped with inlet lenses, and one channeltron. Non-monochromatic Mg Kα radiation was used as excitation source, thanks to a PHI X-Ray source mod. 04-153. AES analysis were performed by a PHI 545 scanning Auger electron system, with a 15-110A cylindrical mirror electron analyser; the electron beam, coming from a coaxial elec-

a) and b) Deconvolution of chromium 2p peak and nitrogen 1s peak of the sample grown at 0.7 mTorr of N₂ partial pressure; c) and d) Deconvolution of chromium 2p peak and nitrogen 1s peak of the sample grown at 2.5 mTorr of N₂ partial pressure.

a) e b) Deconvoluzione del picco 2p del cromo e 1s dell'azoto per il campione cresciuto a una pressione parziale di N₂ di 0.7 mTorr; c) e d) Deconvoluzione del picco 2p del cromo e 1s dell'azoto per il campione cresciuto a una pressione parziale di N₂ di 2.5 mTorr.

tron gun with tungsten emitting filament, had an energy of 5 keV and a sample scanning area of about 0.5x0.5 mm. An Ar^+ ion source (SPECS mod. 12/38) was used for in vacuum cleaning of sample surfaces, prior to chemical composition analysis.
Crystalline structure was determined by a PANalytical X'Pert Pro equipped with a X'Celerator detector, using the Cu $K_α$ radiation at 1.5405 Å. In all scans performed the diffraction angles were calibrated aligning the goniometer on the (004) diffraction angle of Si substrate.
Scanning Electron Microscopy (SEM) images were acquired with a FEI Strata 235 M dual beam system, equipped with a FEG electron source. The nominal electron beam size was 5 nm and accelerating voltage was 15kV.
Nanoindentation was performed by the DI EnviroScope (Veeco) atomic force microscope (AFM) using commercial Berkovich diamond tip mounted on a sapphire cantilever (spring constant 5080 N/m). In order to evaluate the applied load during indentation the AFM photodiode sensitivity was calibrated by standard loading curve and was set to 130 nm/V.
Coatings wear resistance was determined by ball-on-disk tests performed on a CETR UMT-2 tribometer, using a WC ball of 2 mm radius as counterpart. Tests were made at different loads ranging from 0.2 to 1.0 N, corresponding to a maximum Hertzian contact pressure between of 0.7-1.3 GPa respectively. All tests are performed at a fixed rotation speed of 60 rev/min varying the track diameter on the sample surface from 2 to 6 mm.

RESULTS AND DISCUSSION

Fig. 1 a) shows the CrN deposition rate as a function of the N_2 partial pressure. Increasing the N_2 flow, the deposition rate decreases following a nearly linear law from 85 nm/min when no N_2 is used in the deposition chamber, to 35 nm/min for a partial pressure of 2.5 mTorr of N_2. This behaviour is due to the com-

bination of two effects: the lower ionization probability of N_2 molecules with respect to Ar ones, and the reactivity of N_2 on the target surface. As a matter of fact, in reactive magnetron sputtering process, at low N_2 flow rates the nitrogen molecules are incorporated inside the film by Cr atoms coming from the target and then deposited on the substrate surface; in this condition the Ar bombardment of the target is high enough to keep the target surface as pure Cr, and the growth rate is comparable to the case of no N_2 molecules inside the deposition chamber. On the contrary when the N_2 flow is increased, the excess of nitrogen gas in the chamber reacts with the target surface. As a result of the nitridation the yield of sputtered Cr atoms is reduced due to the balance between two competitive effects, i.e., the formation of a CrN layer on the target and the sputtering of this layer due to impinging of the Ar ions [13, 14]. In Fig. 1 a) we also reported the average roughness of the growth samples. The surface topography of the CrN single layer films was measured by AFM; we observed that for all the prepared samples the growth mode is an island growth type with an average grain size of about 50 nm (see Fig. 1 b)). Because these samples are grown keeping the total deposition time constant and since the surface roughness is a function of the total thickness of the films, the average roughness of our samples decreased increasing the N_2 partial pressure, keeping a value smaller than 5 nm.

The amount of nitrogen incorporated inside the film was determined by AES investigations. Since AES is a highly surface sensitive technique, measurement were performed after a surface sputtering at 3 KeV for 5 min with Ar^+ ions in order to remove contaminations of adventitious C atoms. Tab. 1 reports relative concentration of Cr and N in different samples, coming from AES analysis. Two different regimes can be noted: above 1 mTorr, despite the significant change in the N_2 partial pressure, the N/Cr ratio is nearly constant at about 0.77; below 1 mTorr the N/Cr ratio decreases with respect to sample growth at higher flow. Since more than one chemical phase are usually detected in CrN films deposited with a N_2 partial pressure value lower than 20% of process pressure [15-17], XPS analysis were performed to identify CrN chemical phases in samples under study by photoemission peak deconvolution of high resolution scan, taken with analyser pass energy of 50 eV. Since coatings grown at a N_2 partial pressure greater than 1 mTorr have approximately the same N/Cr ratio, the analysis was performed only on one representative sample. Fig. 2 shows the XPS deconvolution of Cr 2p and N 1s peaks for the sample 1 (Fig. 2 a) and Fig. 2 b) respectively) and sample 5 (Fig. 2 c) and Fig. 2 d) respectively).

In such analysis the 2p Cr peak is deconvolved in the five main components corresponding to: metallic Cr (binding energy of 574±0.1 eV), the Cr_2N (574.2±0.1 eV), CrN (575±0.2 eV), Cr_2O_3 (576.5±0.5 eV) and CrO_3 (578.6±0.3 eV) [18]. The N 1s peaks is deconvolved in the contribution given by CrN (596.4±0.2 eV)
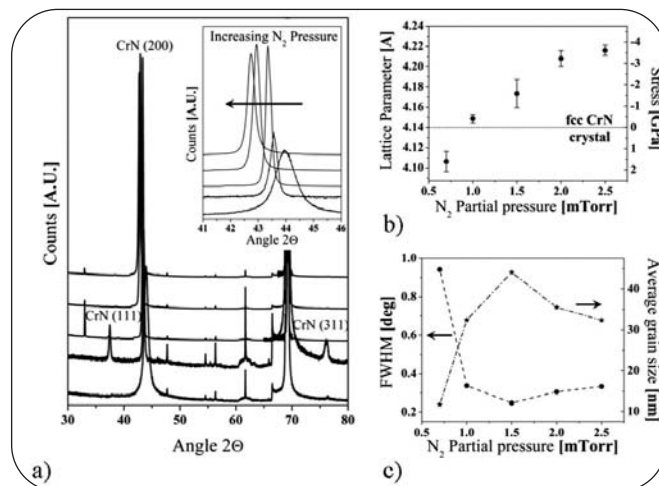
a) XRD scans of CrN coatings. In the inset is reported the effect of the N_2 partial pressure on the (200) CrN Bragg diffraction peak position. b) Variation of the average lattice parameter normal to the sample surface and internal stress as a function of the N_2 partial pressure. c) Variation of the width of (200) diffraction peak and average polycrystalline grain size of the coating as a function of the N_2 partial pressure.
a) Spettri XRD dei rivestimenti di CrN. Nell'inserto della figura è riportato l'effetto della pressione parziale di N_2 sulla posizione del picco di diffrazione di Bragg (200) del CrN. b) Dipendenza del parametro reticolare normale alla superficie del campione e delle tensioni interne al film in funzione della pressione parziale di N_2. c) Variazione della larghezza del picco di diffrazione (200) e della dimensione media del grani policristallini del rivestimento in funzione della pressione parziale di N_2.

and Cr_2N (397.2±0.2 eV) [19]. Comparing the peak intensity of the deconvolved Cr peak one can see that, while the contribution of the chromium oxides is similar between the two samples (~ 35% of the total Cr signal), in sample 1 the amount of Cr_2N is higher than in the case of sample 5. Similar trend can be obtained by the deconvolution of the N 1s peak. In sample 1 Cr_2N peak intensity have almost the same value of the CrN one (Fig. 2 b)), while in the sample 5 the ratio between the peak intensities is about 1/3 (Fig. 2 d)). From XPS analysis we can conclude that samples grown at low partial pressure are a combination of at least two nitride phases (Cr_2N and CrN), while at high pressure the sample stoichiometry is closer to CrN phase.

The structural properties of the chromium nitride films prepared with different N_2 partial pressure was investigated by XRD analysis (Fig. 3 a)). Diffraction lines corresponding to (111), (200)

SAMPLE	N_2 PARIAL PRESSURE	% atomic N	% atomic Cr	N/Cr
1	0.7 mTorr	37	63	0.59
2	1.0 mTorr	44	56	0.78
3	1.5 mTorr	43	57	0.75
4	2.0 mTorr	45	55	0.81
5	2.5 mTorr	43	57	0.75

▲
Tab. 1

Chemical composition of different samples from AES data.
Composizione chimica dei campioni ricavata dall'analisi AES.

and (311) peaks can be observed from XRD patterns that confirms the formation of face centred cubic CrN films during the growth process in the whole range of explored N_2 partial pressure. In contrast to previously reported studies [14-16], there are no evidences of hexagonal Cr_2N phase or metallic Cr phase in the diffraction scans, both in $\psi^2\Theta$ scans and in grazing incidence scans, suggesting the idea that these phases observed by XPS analysis are presents as amorphous structures in our films. From the analysis of the XRD intensities we can deduce that the main texture orientation in the films is the (200) one. The results of the present work agree with the experimental results obtained by Olaya et. al. [10] and by He et al. [20] for the growth of CrN films in similar growth conditions. In these works the preferential texture orientation in the (200) direction is explained in according to the frame of the theory of Petrov et. al. [21] which analyses the microstructural evolution during the film growth. This phenomenological model predicts a change in the texture orientation of a polycrystalline film from (111) to (200) due to the increasing diffusivity of the transition metal adatoms, caused by an high energetic ionic bombardment. In fact for low energy (< 1 eV) ion bombardment, the film evolves on a (111) texture orientation, since N_2 molecules are preferentially chemisorbed on (111) planes, favouring the tapering of metal adatoms in such sites and consequentially increasing the growth velocity of (111) planes. By increasing the energy of N_2 ions to about 20 eV the process to supply atomic nitrogen is changed to a dissociation of the ions caused by the collision with the film surface. In such way nitrogen can be chemisorbed on (200) oriented grains, capturing metal atoms resulting in the development of the (200) texture. The presence of a strong energetic N_2 ions bombardment, during the film growth, is confirmed in XRD analysis of our sample by the shift to lower diffraction angles of the (200) Bragg peak while increasing N_2 partial pressure (see inset in Fig. 3 a)). Such shift demonstrates that the lattice parameter along the normal to the sample surface of the CrN films is not constant, but depends on the growth conditions. A monotonic increase with the partial pressure is measured from XRD data from about 4.10 Å at low N_2 flow up to a nearly constant value of 4.22 Å for higher flow (Fig. 3 b)). Such behaviour suggests the hypothesis of different regimes of in-plan biaxial internal stress inside the films due to point defects generation during the deposition. In fact an in-plan biaxial stress produce a strain in according to the following relation [22]:

$$\varepsilon = \frac{d_{hkl} - d^0_{hkl}}{d^0_{hkl}} = \frac{1-v}{E} \times \sigma$$

(1)

where d_{hkl} is the measured lattice plane distance, d^0_{hkl} is the unstrained lattice plane distance, v and E are the Poisson's ratio and elastic modulus of the material and v is the internal stress. In according to equation (1), a compressive in-plan biaxial stress produce an elongation of the measured lattice parameter along the normal to the sample surface with respect to the bulk value, the opposite effect is produced by a tensile stress. Consequentially the films grown with a N_2 partial pressure smaller than 1 mTorr are in tensile regime, while films grown at higher pressure are subject to a compressive stress, due to the stronger N_2 flow ion bombardment [23].

Fig. 3 c) shows that also the width of the (200) peak is strongly affected by the N_2 partial pressure, pointing out that the coexistence of two nitride phase in the sample 1, produces a nanocrystalline structure with an average grain size of 10 nm calculated with the Scherrer formula [24]. For higher flow, the increasing of the CrN component with respect to Cr_2N phase, produces a narrow XRD (200) peak and consequentially a

greater average grain size. The calculated value of about 35 nm is in good agreement with the size of the structures observed by AFM on the surface (see Fig. 1 b)). The fine crystal structure of the sample grown at lower N_2 flow is also evidenced by SEM imaging, performed on the fractured cross-section of the film. Microstructure evolution through different samples is reported in Fig. 4: at low N_2 partial pressure a fine grain structure without voids corresponding to zone 3 in the Thornton's structural-zone-model is observed (Fig. 4 a)). As pointed out by other authors [25, 26] at low flow of N_2 the local epitaxial growth, typical of polycrystalline films, is prevented by the presence of more than one phase (i.e. Cr, CrN_2, CrN) in the film. In such regime the film growth proceeds trough a continuous renucleations, producing the disruption of the columnar structure. Increasing the N_2 partial pressure, the structure evolves in a not well defined columnar form (Fig. 4 b), 4 c)). A further increase of the N_2 partial pressure produces a fully dense fibrous structure, having almost equiaxed grains and a structure equivalent to zone 2 of the Thorton's model, in this regime the film growth is dominated by significant surface diffusion of adatoms, which is sufficient to cause local epitaxy within the individual columns [10, 20, 27].

Nanoindentation experiments have been carried out on the whole range of samples produced, in order to evaluate micro hardness. Due to the different thickness of the coatings, in order to avoid any influence of the substrate, the maximum load was set to 1.3 mN. In such a way the maximum penetration depth during indentation was a tenth of the coating total thickness.

Tab. 2 resumes the average value of the hardness on a set of 36 indentations performed on the sample surface. No clear trend is observed above this value, and the experimental error of the measurements does not allow us to ascertain the influence of the different phases and microstructures on the hardness of the films. The presence of an high density of structural defects inside our coatings can partially hide the effect of different microstructures on the hardness of the material, however the average value of about 17 ± 2 GPa is comparable to previously reported hardness of sub-stoichiometric CrN coatings growth without applying a substrate voltage [25]. Even if no clear trend in the hardness of different materials was observed as a function of N_2 partial pressure, ball on disc tests revealed that wear rates are strongly affected by N_2 partial pressure during deposition process. AFM images of the traces on the samples surface after a sliding test against a WC ball at a normal load of 0.2 N are reported in Fig. 5 a) and 5 b). The line profile (Fig. 5 c)) shows that the worn surface is larger for sample grown at lower N_2 partial pressure with respect to the sample grown at higher N_2 pressure. A general reduction trend in

SAMPLE	N₂ PARIAL PRESSURE	Average Hardness
1	0.7 mTorr	18 ± 2 GPa
2	1.0 mTorr	17 ± 2 GPa
3	1.5 mTorr	16 ± 2 GPa
4	2.0 mTorr	16 ± 1 GPa
5	2.5 mTorr	19 ± 1 GPa

▲
Tab. 2

Hardness value measured for different samples.
Durezza misurata dei differenti campioni analizzati.
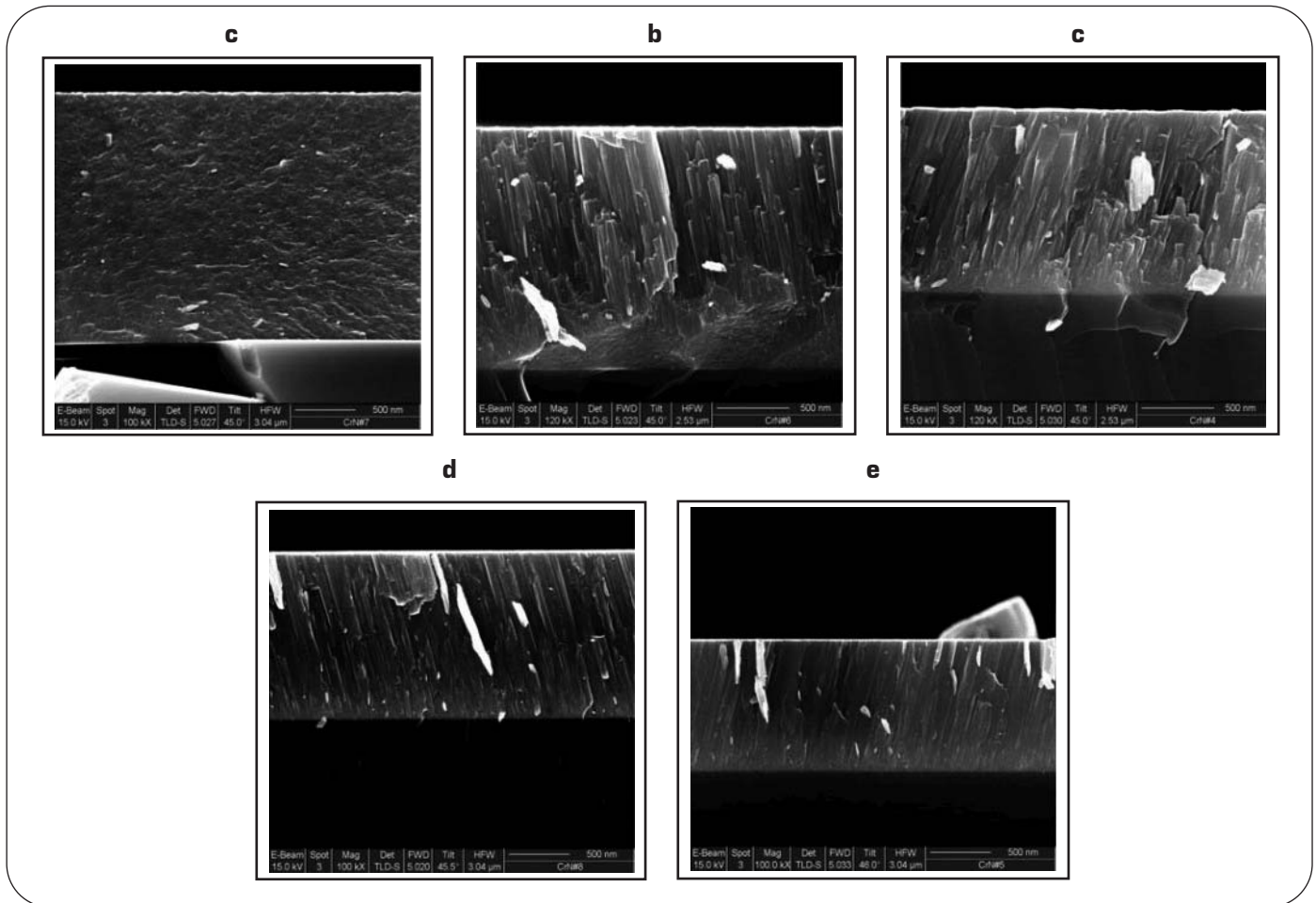
▲
Fig. 4

SEM images of the coating microstructure as a function of the N₂ partial pressure. a) 0.7 mTorr, b) 1.0 mTorr, c) 1.5 mTorr, d) 2.0 mTorr, e) 2.5 mTorr.

Immagini SEM della microstruttura del film in funzione della pressione parziale di N₂. a) 0.7 mTorr, b) 1.0 mTorr; c) 1.5 mTorr; d) 2.0 mTorr; e) 2.5 mTorr.

the wear rate of the film as a function of the N_2 partial pressure is reported in Fig. 5 d); the wear rate change from an average value of $8.0 \pm 0.9 \times 10^{-7}$ mm³/(N m) for sample 1 to $8 \pm 5 \times 10^{-8}$ mm³/(N m) for sample 5. Those results can not be explained only in terms of difference of chemical composition or hardness between the samples. They are instead correlated with the internal stress of the coatings (see Fig. 3 b)). This parameter affects the wear rate of such films in agreement with a recent study reported by van Essen et al. [28]. As a matter of fact, comparing Fig. 3 b) and Fig. 5 d), the samples with higher compressive stress have a lower wear rates if compared with the samples with smaller internal stress. This suggests that an high level of compressive stress reduce the chip production during sliding.

CONCLUSIONS

In this work we characterised CrN films deposited at high deposition rate (> 1 μm/h) produced in magnetron sputtering systems at different partial pressures of N_2 reactive gas. XRD analysis reveals the formation of cubic CrN films in the whole range of studied partial pressures, with different internal stress. The stress distribution progressively changes from tensile to compressive increasing the N_2 partial pressure due to the increasing energy of N_2^+ ion bombarding. XPS and AES analyses point out that at low N_2 flow the film is composed by a mixture of Cr_2N and CrN, while at higher partial pressure the main phase presents inside the coating is CrN. The presence of mixed CrN and Cr_2N have a detrimental effect on the microstructural evolution of the growth process, preventing the development of a well aligned columnar structure inside the film. This negative effect is related to the continuous renucleation of the two phases during the growth. The mechanical properties of these coatings have also been considered and, even if a clear trend of the film hardness has not been observed in the range of studied pressures, the wear rate has an interesting behaviour, decreasing by an order of magnitude if the internal stress switches from tensile (small value of N_2 partial pressure) to compressive (high value of N_2 partial pressure).

REFERENCES

[1] R.F. Bunshah, Handbook of hard coatings, editor Noyes Publication/William Andrew Publishing, LLC Norwich, New York, USA (2001).

[2] P. Hones, N. Martin, M. Regula and F.Lévy, J. Phys. D, 36, 1023-1029 (2003).

[3] H. Holleck, J. Vac. Sci. Technol. A, 4, 2661-2669 (1986).

[4] F. Quesada, A. Mariño and E. Restrepo, Surf. and Coat. Technol., 201, 2925-2929 (2006).

[5] B. F. Chen, W. L. Pan, G. P. Yu, J. Hwang and J. H. Huang, Surf. and Coat. Technol., 111, 16-21 (1999).

[6] B. Navinšek, P. Panjan and I. Milošev, Surf. and Coat. Technol., 97, 182-191, (1997).

[7] P. Panjan, B. Navinšek, A. Cvelbar, I. Milošev and A. Zalar, Thin Solid Films, 281-282, 298-301 (1996).

[8] F. Esaka, K. Furuya, H. Shimada, M. Imamura, N. Matsubayashi, H. Sato, A. Nishijima, A. Kawana, H. Ichimura, and T. Kikuchi, J. Vac. Sci. Technol. A 15, 2521 (1997).

[9] J. Musil, Surf. and Coat. Technol., 125, 322-330 (2000).

[10] T. Hurkmans, D. B. Lewis, J. S. Brooks and W. -D. Münz, Surf. and Coat. Technol., 86-87, 192-199(1996).

[11] J.A. Thornton, Annu. Rev. Mater, 7, 239 (1997).

[12] J.J. Olaya, S.E. Rodil, S. Muhl, and L. Huerta, Surf. and Coat. Technol., 200, 5743-5750 (2006).

[13] J.L. Vossen and J.J. Cuomo, Glow discharge sputter deposition in: Thin film processes – J.J. Vossen and W. Kern Academic Press, Inc. (1978).

[14] R. Mientus and K. Ellmer, Surf. and Coat. Technol., 116-119, 1093-1101 (1999).

[15] G.Wei, A. Rar, J.A. Barnard, Thin Solid Films, 398-399, 460-464 (2001).

[16] Kyung H. Nam, Min J. Jung and Jeon G. Han, Surf. Coat. Technol. 131, 222-227 (2000).

[17] S.M. Aouadi, T.Z. Gorishnyy, D.M. Schultze and S.L. Rohde, Surf. Coat. Technol. 153, 1-9 (2002).

[18] The reported the energy position of Cr compounds are taken as the average of following the reported peak position: Esaka et. al. J.Vac. Sci. Technol. A 15(5) 2521 (1997), A. Lippitz et. al. Sur. & Coat. Techn. 200, 250 (2005), C. Palacio et al. Thin Solid Film 513, 175 (2006), Riviere et. al. J.Appl. Phys. 10 6361 (2002), R. Sanjines et al. Thin Solid Films 332, 225, (1998), Milosev et. al. Thin Solid Film 303, 246, (1997).

[19] The reported the energy position of N compounds are taken as the average of following the reported value: Esaka et. al. J.Vac. Sci. Technol. A 15(5) 2521 (1997), A. Lippitz et. al. Sur. & Coat. Techn. 200, 250 (2005), C. Palacio et al. Thin Solid Film 513, 175 (2006), R. Sanjines et al. Thin Solid Films 332, 225, (1998).

[20] Xiao-Ming He, N. Baker, B. A. Kehler, K. C. Walter, M. Nastasi, and Y. Nakamura, J. Vac. Sci. Technol. A 18, 30-36 (2000).

[21] I. Petrov, P. B. Barna, L. Hultman, and J. E. Greene, J. Vac. Sci. Technol. A, 21, S117-S128 (2003).

[22] L.D. Landau, E.M. Lifschitz, Theory of Elasticity, 3rd ed., Pergamen Press, Oxford, 1986.

[23] To extimate the internal stress of the growth film we have used a value of E = 280 GPa and v = 0.3: R. Hoy, W.G. Sloof and G.C.A.M. Janssen Surf. and Coat. Technol., 179, 215-222 (2004).

[24] H.P. Kluge and L.E. Alexander, X-ray Diffraction Procedures (2nd ed.), John Wiley, New York (1974).

[25] Zenghu Han, Jiawan Tian, Qianxi Lai, Xiaojiang Yu and Geyang Li, Surf. Coat. Technol., 162, 189-193 (2003).

[26] P. Hones, R. Sanjines and F. Levy, Surf. Coat. Technol., 94-95, 398-402, (1997).

[27] P. J. Kelly and R. D. Arnell, J. Vac. Sci. Technol. A, 16, 2858-2869 (1998).

[28] P. van Essen, R. Hoy, J.-D. Kamminga, A.P. Ehiasarian and G.C.A.M. Janssen, Surf. Coat. Technol., 200, 3496-3502 (2006).

ABSTRACT

INFLUENZA DELLA PRESSIONE PARZIALE DI AZOTO NELLA CRESCITA DI RIVESTIMENTI DI NITRURO DI CROMO

Parole chiave: Magnetron sputtering reattivo, nitruro di cromo, usura, XRD, XPS, AES

In questo lavoro si è studiato il processo di deposizione di nitruro di cromo tramite magnetron sputtering reattivo al variare della pressione parziale di azoto durante la crescita. Tenendo costante la pressione totale durante la deposizione a un valore di 3.0 mTorr, il rapporto tra i gas di processo N₂ e Ar è stato fatto variare da 0.3 a 5.0, per favorire la crescita di film con differenti microstutture. Le analisi SEM effettuate hanno evidenziato che la microstruttura dei film depositati dipende dalla pressione parziale di azoto utilizzata durante la crescita. In particolare una bassa pressione parziale di azoto favorisce la formazione di un film con una struttura granulare, mentre una struttura colonnare compatta si sviluppa ad alte pressioni parziali. Tramite l'analisi AES e XPS si è potuto rilevare che la formazione della struttura granulare è dovuta alla coesistenza di differenti fasi di nitruro di cromo (CrN e Cr₂N) nel film. Queste fasi provocano a livello microscopico una continua rinucleazione dei grani di crescita, impedendo la formazione di una struttura colonnare densa. Le differenti pressioni parziali di azoto utilizzate durante la crescita non solo influenzano la microstruttura del film, ma hanno anche un importante effetto sullo stato di deformazione residuo interno del film e sulle proprietà tribologiche del rivestimento. L'analisi XRD effettuata ha messo in evidenza che le tensioni residue cambiano da un regime tensile a un regime compressivo, all'aumentare del rapporto N₂/Ar durante la deposizione, a causa dell'aumento del bombardamento ionico che il film subisce durante la crescita. Questo aumento dello sforzo residuo compressivo riduce di un ordine di grandezza il tasso di usura del materiale