

Characteristics of silicon doped chromium nitride coatings produced by magnetron sputtering: the influence of processing parameters

L. CUNHA* , C. MOURA

Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Silicon doped chromium nitride thin films have been deposited by r.f. reactive magnetron sputtering. The effect of processing parameters, namely the nitrogen partial pressure in the working atmosphere and the power density applied to the Si target, on the properties on the films structure and mechanical properties has been investigated. X-ray diffraction (XRD) was used to analyze the crystalline phases, crystal orientation/texture, size and micro-stress state of the produced films. The mechanical properties, namely the hardness, and resistance to plastic deformation were obtained by nanoindentation. These studies allow establishing relations between the characteristics of the films. The results showed that all the coatings present a face-centered cubic (fcc) CrN structure, with (111) preferred orientation. The calculated grain size is between 13 and 18 nm. The highest measured hardness was around 34 GPa for a film produced with produced with the lowest nitrogen flow rate.

Keywords: CrSiN, Reactive Sputtering, Structure, Mechanical properties

1. Introduction

The silicon addition to transition metal nitrides (TMN), gives origin to grain refinement due to the formation of nanocomposite structures of nanocrystallite (n) TMN grains in an amorphous (a) Si_3N_4 matrix [1-11] and improves the mechanical properties [1,2,5-7]. There is still discussion to be done on the structure and mechanical properties resultant from the addition of silicon to chromium nitride films. There are studies about the structure, the electrical, optical and mechanical properties of such films [8,12], inclusively the effect of the concentration of silicon [13,14]. The structure of the films produced changed from a solid solution for lower silicon concentration to a nanocomposite structure, for higher concentrations [13]. It was also registered a decrease of grain size with the increase of silicon content, and a gradual change of structure from crystalline to amorphous [14]. In these works, the way the hardness and Young's modulus varied was not evident tendency. Two other studies refer the production of CrSiN coatings, by sputtering, but using Si cuppons on the erosion zone of the Cr target [15-16] and the obtained maximum hardness, measured by nanoindentation, was around 30 GPa [16].

In this paper, CrSiN films were produced by reactive magnetron sputtering, using a radiofrequency power source. The main objective of this work is to study the effect of the deposition conditions and of the effect of addition of silicon atoms on the chromium nitride structure on the mechanical properties of the coatings.

2. Experimental details

The coatings were deposited by reactive r.f. magnetron sputtering on stainless steel (AISI 314) substrates. The substrates were previously ultra-sonically cleaned in acetone and sputter etched in a pure argon atmosphere. The coatings were synthesized using pure targets: a Cr target, with 200 mm diameter and a Si target, with 76 mm diameter. The deposition time, for all the samples was 18000 s. The coatings were deposited in a rotation mode (constant frequency of 4 rpm) and will be known as CrSiN from this point all over the article.

The working atmosphere was constituted by argon and nitrogen. The argon flow was kept constant (60 sccm), but the nitrogen flow rate varied from 13.7 to 47.8 sccm. The power applied to the Cr target was maintained constant (500 W) and the power applied to the Si target varied between 0 and 125 W. The substrate holder was maintained at a distance of 65 mm form the target and was connected to a DC power source. All the coatings were deposited onto the substrates with an applied bias voltage of -50 V. The substrate temperature during deposition was 400°C except ine of the coatings that was deposited at 300 °C.

The thickness of the coatings was obtained by ball cratering. The composition was obtained by Rutherford backscattering spectroscopy (RBS). Table 1 presents the deposition conditions and the thickness of the coatings.

Table 1. Deposition conditions and thickness of the obtained CrSiN coatings: P_{Si} – RF power applied to the Si target; T – Substrate temperature; t – Deposition time; $\Phi(N_2)$ – Nitrogen flow rate; t_c – thickness.

Sample	P_{Si} (W)	T (°C)	$\Phi(N_2)$ (sccm)	t_c (μm)
A1	100	400	13.7	1.5
A2	100	400	17.8	1.4
A3	100	400	27.8	1.0
A4	100	400	33.7	1.2
AB5	100	300	37.8	1.3
A6	100	400	47.8	1.0
B7	50	400	37.8	1.3
B8	75	400	37.8	1.1
B9	125	400	37.8	1.2

X-ray diffraction (XRD) patterns were obtained in a Philips PW 1710 equipment, with a classical $\theta/2\theta$ Bragg-Brentano configuration, using Cu $K\alpha$ radiation. The grain size and the micro-stress state of the crystallites was calculated by fitting the XRD peaks by a pseudo-Voigt function [17]. This method needs only a diffraction peak and is based on the fact that the experimental profile is the convolution of structural and experimental profiles. The crystallite size calculations were performed by making corrections due to the Cu $K\alpha_2$ component and instrumental profile.

The nano-hardness and Young's modulus perpendicular to the surface of the coatings were obtained by using a microprobe, equipped with a Berkovich diamond indenter, with instrumented indentation depth of 100 nm. The load measurement resolution was better than 1 mN. The hardness and Young's modulus were calculated using the Oliver and Pharr method [18].

3. Results and discussion

3.1 Deposition process and composition

The deposition conditions chosen for this study were decided as result of previous results of chromium nitride coatings depositions [19]. In the referred work the authors found the deposition parameters to obtain chromium nitride coatings with a Cr:N 1:1 stoichiometry. This ratio was obtained for all the coatings produced with a nitrogen flow rate equal or higher than 20 sccm, but the CrN phase was already detected with a 10 sccm N_2 flow rate. All CrSiN films of this work were prepared with N_2 flow rates higher than 13.5 sccm, but it was decided to produce two groups of films with systematic variation of only one of the deposition parameters, maintaining the remaining parameters constant: i) group A - produced varying the N_2 flow rate, from 13.7 to 47.8 sccm (in Table 1, these samples are identified by letter A and a number); ii)

group B - produced varying the power applied to the Si target, from 50 to 125 W (in Table 1, these samples are identified by letter A and a number). Note that one of the presented samples belongs to both groups, and is identified as AB5. All the coatings showed a N/Cr ratio close to 1. The Si concentration on these samples was found to be always lower than 5%. It is well known that, with so low concentration, by RBS, it is not possible to establish rigorous information about the concentration. For so low levels of concentration the error may reach 2%. Because of this fact, the Si concentration of each coating is not presented. The coatings may be considered as Si doped chromium nitride coatings.

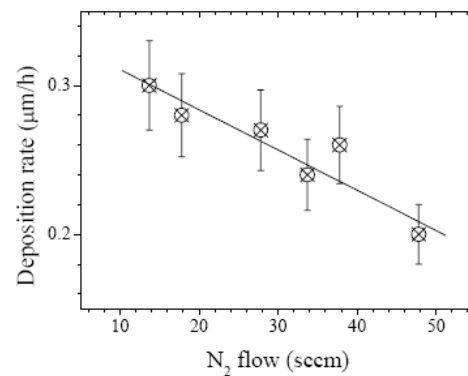


Fig. 1a) Deposition rate of CrSiN coatings, as function of nitrogen gas flow.

Fig. 1 shows the variation of the deposition rate as function of the reactive gas flow rate (Fig. 1a)) and as function of the power applied to Si target (Fig. 1b)). Both groups present a relatively low deposition rate, but should be taken into account that, in rotation mode configuration (dynamic substrate holder), the substrate is directly in front of the targets during only part of the total period of rotation (around 20% of the time).

For samples of group A, the deposition rate decreases, from around 0.3 to about 0.2 $\mu\text{m/h}$, with the increase of the N_2 flow rate. Previous work showed that to produce stoichiometric CrN coatings there would be no need to use N_2 flow rates higher than 20 sccm [19]. The excess of this gas in the deposition chamber increases total pressure and promotes the target poisoning effect, and in consequence, a systematic decrease of the deposition rate, as observed in figure 1a). Anyway producing films with higher N_2 flow rates, allow to understand the way some characteristics change. The group B CrSiN samples, produced with variable power applied to Si target, didn't show a systematic variation of the deposition rate (average around 0.24 $\mu\text{m/h}$).

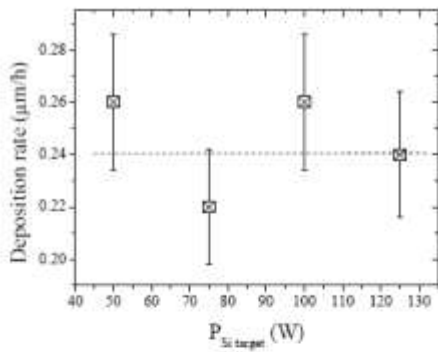


Fig. 1b) - Deposition rate of CrSiN coatings, as function of power applied to the Si target.

3.2 Structure

The XRD patterns of all produced samples show unequivocally the presence of CrN crystals. The XRD patterns of the CrSiN coatings produced with increasing N_2 flow, reveal the presence of the fcc CrN phase with (111) preferred orientation, although small peaks corresponding to (200), (220), (311) and (222) directions were detected. It was not detected any diffraction peak that could be assigned to silicon or silicon nitride.

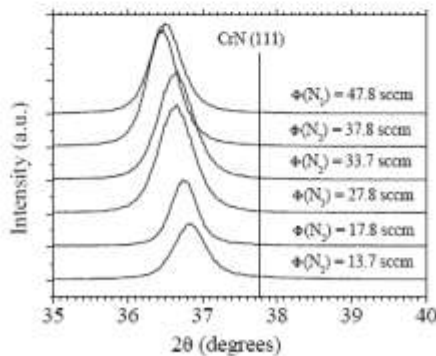


Fig. 2. XRD patterns of group A samples.

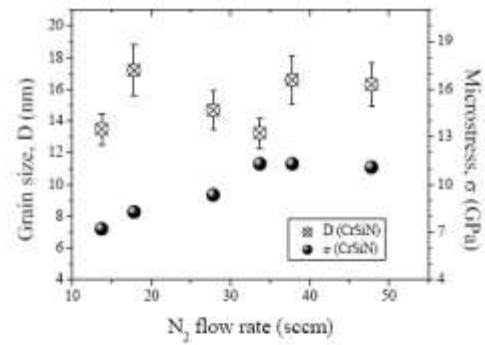


Fig. 3. Variation of grain size and of the micro-stress of CrN crystallites of A samples.

Observing the evolution of CrN (111) peak for the A samples (fig. 2), it is noticed a systematic shift to lower diffraction angles, meaning a systematic increase of the lattice parameter due to the progressive insertion of N atoms in the CrN structure. This results in an increase of the strain and, in consequence, of the microstress state of the crystallites (fig. 3). The results presented in this figure were obtained by fitting (111) CrN diffraction peaks by a pseudo-Voigt function [17]. It is detected a superior limit for the micro-stress, reached at a 33.7 sccm N_2 flow ($a = 0.4264 \text{ nm}$; $\sigma = 11.3 \text{ GPa}$). The variation of the grain size, as function of the reactive gas flow, doesn't follow a systematic variation.

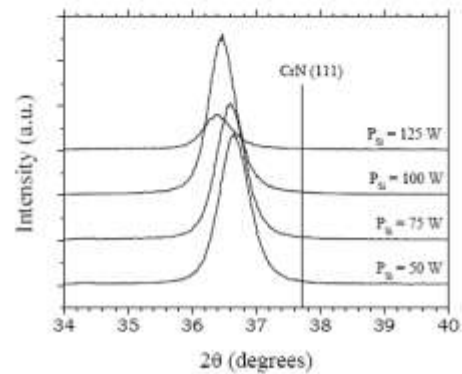


Fig. 4. XRD patterns of B samples.

In the case of the group B samples, it is noticed a regular shifting of the CrN (111) peak to lower angular positions with the increase of the power applied to the Si target (fig. 4). As the coatings are produced in conditions of obtaining CrN stoichiometry, the increase of Si content may promote an increase of the insertion of Si atoms in CrN structure, and in consequence an increase of the lattice parameter and microstress (fig. 5).

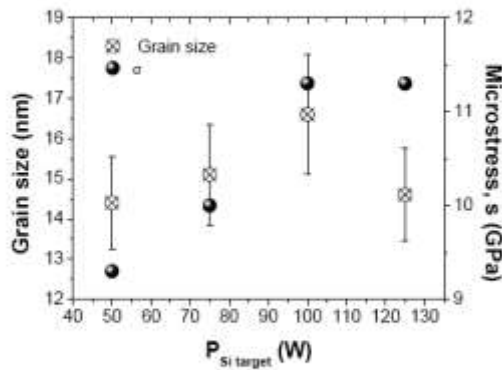


Fig. 5. Variation of grain size and micro-stress in CrN crystallites in B samples.

The variation of the lattice parameter, and as consequence of the microstress, of CrN crystallites, with the increase of the nitrogen flow and the increase of the power applied to de Si target (increase of the Si content) may be evidenced and summarized in figure 6.

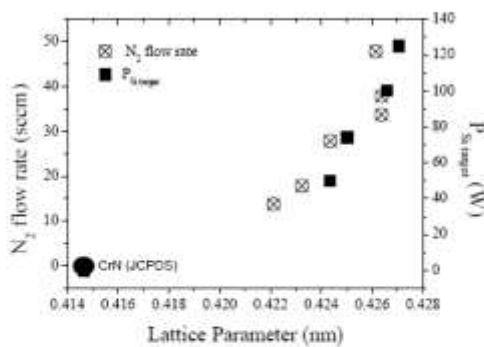


Fig. 6. Variation of the lattice parameter of all CrSiN samples.

3.3 Mechanical properties

The highest hardness (34 GPa) was obtained for the samples produced with lowest nitrogen flow and with highest power applied to the Si target (Fig. 7a and b).

Looking to the graphs containing the information about the grain size, it is noticed that the highest hardness, for each group of CrSiN coatings, coincides with the samples with lowest grain size (around 13.5 nm for the samples of group A and around 14.5 for samples of group B). The highest hardness of silicon doped metal nitride coatings is obtained for coatings with a certain concentration of Si [1,4,20,21].

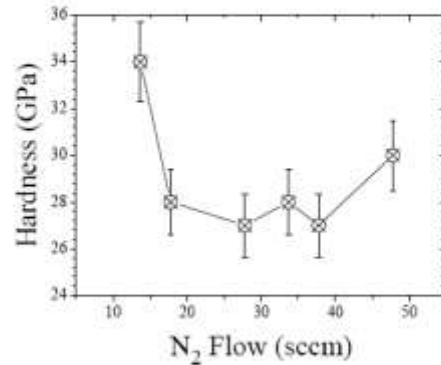


Fig. 7a) Variation of the hardness of A samples.

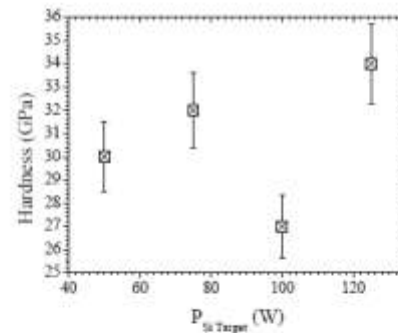


Fig. 7b) Variation of the hardness of B samples.

Below and above a certain Si concentration, the hardness decreases. This behaviour is confirmed when the hardness of CrSiN coatings is compared with the hardness of CrN coating produced in similar conditions. CrSiN coatings are harder than CrN coatings for nitrogen flows between 10 and 15 sccm, and softer for nitrogen flow higher than 30 sccm. Between 15 19 and 30 sccm, the hardness is similar [19].

Between the limits of the power applied to the Si target, it is noticed a general increase of hardness with the increase of the power applied, but there is an exception for the sample produced with 100 W. The main reason that may justify this anomalous behaviour is the substrate temperature during deposition. This particular sample was produced with a temperature 100 °C lower than the other samples.

In terms of resistance to plastic deformation, obtained by the ratio between the square of the hardness and the cube of the Young's modulus (H^2/E^3), it is clear that this resistance decreases with the increase of the nitrogen gas flow (fig. 8a), and as consequence with the increase of the hardness and increase of the microstress.

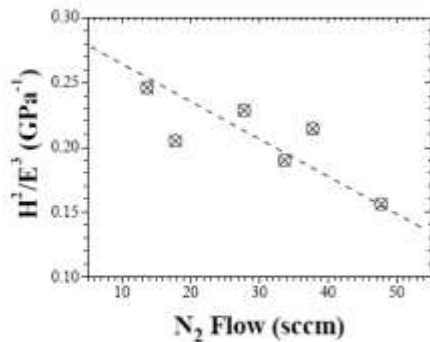


Fig. 8a) - Resistance to plastic deformation as function of A samples (the dashed line is only to guide the eye)

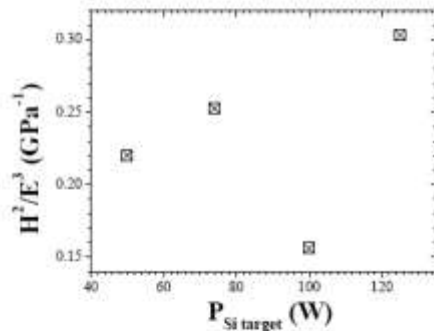


Fig. 8b) Resistance to plastic deformation as function of B samples.

Looking to the variation of this ratio with the power applied to the Si target, it seems that, within the limits of Si concentration lower than 5%, the increase of the Si content increases the resistance to the plastic deformation of the CrSiN coatings (figure 8b).

4. Conclusions

Two groups of CrSiN coatings were produced by reactive magnetron sputtering. The main results may be summarized as follows:

- All the CrSiN samples showed a N/Cr ratio close to 1. The Si concentration on these samples was found to be always lower than 5%.
- All the coatings evidenced a face-centered cubic (fcc) CrN structure, with CrN (111) preferred orientation.

Could not be detected diffraction peaks that might be assigned to silicon or silicon nitride.

- The CrN diffraction peaks suffer an increasing shift to lower angles with the increase of the reactive gas flow and with the increase of power applied to de Si target;

- The systematic increase of the lattice parameter with the increase of the nitrogen flow and with the power applied to the Si target results in a systematic increase of the strain and, in consequence, of the microstress of the CrN crystallites;

- The grain size of CrN crystallites varies between 13 and 18 nm;

- The hardest samples were those with smallest grain size;

- The resistance to plastic deformation decreases with the increase of the nitrogen gas flow and with the decrease of the power applied to de Si target.

Acknowledgements

The authors gratefully acknowledge Kaj Pischow for the nanoindentation determinations and Dr. Luis Rebouta for the RBS measurements.

References

- [1] S. Veprek, S. Reiprich, Thin Solid Films **268**, 64 (1995)
- [2] G.-S. Kim, B.-S. Kim, S.-Y. Lee, Surf. Coat. Technol. **200**, 1814 (2005)
- [3] M. Diserens, J. Patscheider, F. Lévy, Surf. Coat. Technol. **108-109**, 241 (1998)
- [4] S. Veprek, J. Vac. Sci. Technol. A **17**, 2401 (1999)
- [5] H.C. Barshilia, A. Jain, K.S. Rajam, Vacuum **72**, 241 (2004)
- [6] G.A. Zhang, Z.G. Wu, M.X. Wang, X.Y. Fan, J. Wang, P.X. Yan, Appl. Surf. Sci. **253**, 8835 (2007)
- [7] J.H. Park, W.S. Chung, Y.-R. Cho, K.H. Kim, Surf. Coat. Technol. **188-189**, 425 (2004)
- [8] E. Martinez, R. Sanjines, A. Karimi, J. Esteve, F. Levy, Surf. Coat. Technol. **180-181**, 570 (2004)
- [9] D. Pilloud, J.F. Pierson, J. Takadoum, Thin Solid Films **496**, 445 (2006)
- [10] Y.S. Dong, Y. Liu, J.W. Dai, G.Y. Li, Appl. Surf. Sci. **252**, 5215 (2006)
- [11] Q. Liu, Q.F. Fang, F.J. Liang, J.X. Wang, J.F. Yang, C. Li, Surf. Coat. Technol. **201**, 1894 (2006)
- [12] E. Martinez, R. Sanjines, O. Banakh, F. Lévy, Thin Solid Films **447-448**, 332 (2004)
- [13] H.Y. Lee, W.S. Jung, J.G. Han, S.M. Seo, J.H. Kim, Y.H. Bae, Surface & Coatings Technology **200**, 1026 (2005)
- [14] G. Zhang, L. Wang, S.C. Wang, P. Yan, Q. Xue, Applied Surface Science **255**, 4425 (2009)
- [15] D. Mercs, N. Bonasso, S. Naamane, Jean-Michel Bordes, C. Coddet, Surface & Coatings Technology **200**, 403 (2005).

- [16] D. Meres, P. Briois, V. Demange, S. Lamy, C. Coddet, *Surface & Coatings Technology* **201**, 6970 (2007)
- [17] Th.H. de Keijser, J.I. Langford, E.F. Mittemeijer, A.B.P. Vogels, *J. Appl. Crystallogr.* **15**, 308 (1982)
- [18] W.C. Oliver, G.M. Pharr, *J. Mater. Res.* **7**, 1564 (1992)
- [19] L.Cunha, C. Moura, submitted to *Journal of Nano Research* (2010).
- [20] F. Vaz, L. Rebouta, P. Goudeau, J. Pacaud, H. Garem, J. P. Riviere, A. Cavaleiro, E. Alves, *Surf. Coat. Technol.* **133**, 307 (2000)
- [21] F. Vaz, L. Rebouta, B. Almeida, P. Goudeau, J. Pacaud, J. P. Riviere, J.B.E. Sousa, *Surf. Coat. Technol.* **120**, 166 (1999)