Residual stress, mechanical and microstructure properties of multilayer Mo_2N/CrN coating produced by R.F Magnetron discharge

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A B S T R A C T

We have investigated the effect of the period thickness of the multilayer Mo_2N/CrN deposited on Si substrate produced by reactive magnetron sputtering. Mo_2N presents a face centered cubic structure and CrN an orthorhombic one. The residual stress of the coatings was determined by the measurement of the substrate curvature. The microstructure of the multilayer was investigated from the X-ray diffraction and scanning electron microscopy (cross section images). The residual stresses resulting from the deposition of the different bi-layer thickness were measured and correlated to the structural properties of the coating as well as the nanoindentation analysis of the coating. The stresses are compressive and tensile for the individual Mo_2N and CrN layer respectively. The result shows that an increase of the multilayer coatings Mo_2N/CrN thicknesses induce an increase of the hardness and the elastic modulus, in the other hand the tensile stress increases. The shift of the XRD diffraction peak (1 1 1) of Mo_2N at high angle which means the reduction of the residual stress is in good agreement with the residual stresses measurements.

1. Introduction

Thin films have been widely applied to microelectronic, opto-electronic, anti-wear and anti-corrosion coating, and many other industries. The transition metal nitride coatings prepared by PVD exhibit good mechanical and tribological properties and are applied as protective coatings in industrial applications [1].

In multilayer coatings the interfaces have an important effect on the mechanical properties. Hence, the different shear modulus of the layers constitutes a barrier limiting or preventing the movement of the dislocations. Additionally, at grain boundaries, deflection and/or distribution of dislocations and cracks can occur, which leads to an increase in the resistance of the coating [2]. The compressive residual stress has been reported to promote adhesion by the increase of the resistance against tensile crack failure [3].

Residual stress in the thin films has a great influence on the full process of design, fabrication and package of the devices [4], and thus is an extremely important parameter in PVD coatings [5]. The presence of interfaces in multilayer thin films, which causes interface stress and strain, is the most common and fundamental issue in hardness enhancement in nano-multilayer thin film [6].

Gilewicz et al., have found an improvement of the hardness and the coefficient of friction in the multilayer coatings Mo_2N/CrN in comparison to the individual layers CrN and Mo_2N, the coatings Mo_2N/CrN are characterized by a hardness above 25 GPa and the lowest coefficient of friction of 0.4 [7]. Koshy et al. [8] successfully deposited Mo_2N/CrN coatings and investigated the effect of the temperature. The multilayer coatings show a temperature activated self-lubricating mechanism due to the oxidation of MoO_3 at high temperatures. The multilayered TiN/CrN was found to have superior properties to both homogenous TiN and CrN [9,10]. Stueber et al., also reported that deposition at low substrate temperatures or increasing substrate bias, results in the growth of polycrystalline multilayer structures which often show a hardness improvement with bilayer modulation periods in the range of 2–10 nm [2].

In the present paper, we combine thin layers of molybdenum nitride (Mo_2N) with compressive residual stress and chromium nitride (CrN) with tensile stress and investigated the Mo_2N/CrN multilayered coatings with different bi-layer periods form 185 nm to 220 nm. A correlation between the mechanical properties (i.e. hardness, elastic modulus and stress) and the microstructural properties of the Mo_2N, CrN and multilayer coatings has been found.

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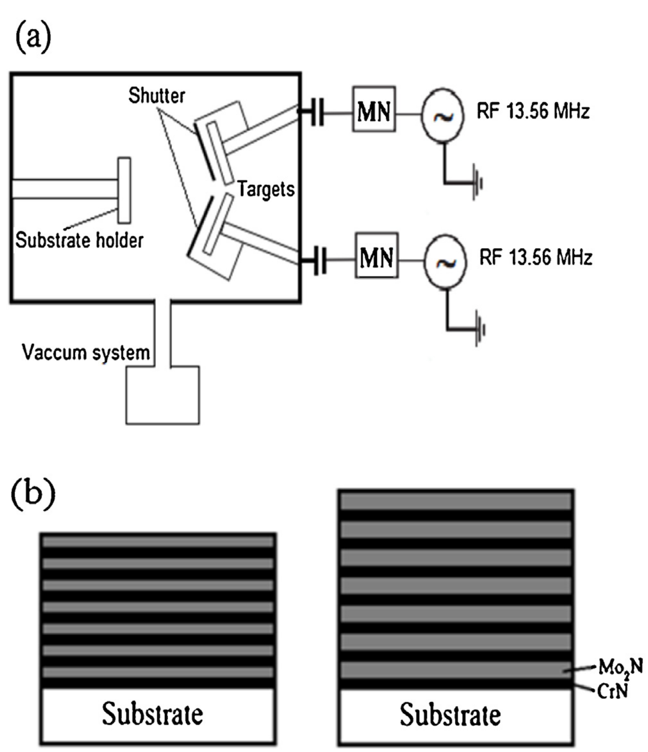

Fig. 1. (a) Sputtering system, (b) schematic description of the multilayer configurations.

Table 1
Thicknesses of the multilayers.

Total thickness (μm)	CrN thickness (nm)	Mo_2N thickness (nm)	Bi-layer thickness (nm)
1.30	93	93	186
1.54	93	127	220

2. Experimental

Multilayer Mo_2N/CrN coating was deposited by R.F (13.56 MHz) reactive magnetron sputtering in a NORDIKO 3500 system. The targets are 100 mm diameter disks of pure molybdenum and chromium. Both targets are in a confocal configuration with a target to substrate distance of 160 mm and an angle of ±30° between the substrate normal and the targets one (Fig. 1(a)). The discharge power was set at 250 W and 400 W for molybdenum and chromium respectively. The absolute working pressure was fixed at 5×10^{-3} mbar, while the nitrogen partial pressure was 1.5×10^{-3} mbar. The nitrogen partial pressure was optimized for both targets before synthesizing the Mo_2N/CrN multilayer films. For the multilayer, 7 bi-layers are deposited with a constant CrN thickness and two Mo_2N thicknesses (Fig. 1(b)). For both multilayered coatings the deposition sequence started with the deposition of a thin chromium layer followed by 93 nm of CrN. The thicknesses of each sublayer are summarized in Table 1.

All depositions were performed on (1 0 0) silicon substrate (380 μm thick). Film thickness was determined by a Wyko profilomter NT 1100, which was also used to obtain the images of the substrate curvature after and before coating. The values and directions of the radii of the coating curvature were obtained by "Gwyddion". The microstructure was analyzed by scanning electronic microscopy (JEOL JSM-5900 LV) and X-ray diffraction (Philips Model X'Pert) using Cu Kα X-ray. To measure elastic modulus and hardness, nanoindentation measurements were performed on a Nano Instrument Berkovich indenter in a Continuous Stiffness Measurement mode.

3. Results and discussion

3.1. Microstructure

Fig. 2 shows the cross section of the individual and multilayer Mo_2N/CrN coating on silicon substrates. All the samples present a columnar structure. The molybdenum nitride film seems to be denser than the chromium one and a tilt of about 10° is observed for this last coating; probably due to the target inclination (Fig. 2(a) and (b)). This is consistent with the working pressure and the target inclination angle [11].

In Fig. 2(c) and (d), the seven bi-layers, for a total thickness of 1.30 and 1.54 μm respectively, can be easily observed. Dark layers correspond to CrN and light layers correspond to Mo_2N and a coherent columnar growth of the multilayer is observed. The interfaces are clearly defined near the substrate but seem to vanish when approaching the surface of the coatings. The origin of this phenomenon could be found in the increase of roughness with the thickness.

Fig. 3 shows the X-ray diffraction spectra with a glancing angle ($\omega = 2°$) of layers Mo_2N, CrN and Mo_2N/CrN thin films with different thickness on silicon. The XRD patterns reveal that all the films are polycrystalline.

Taking account of the standard reference sample listed in (00-025-1366) and (03-065-6914) PDF database, the films can be assigned to the Mo_2N phase in face centered cubic structure and CrN in orthorhombic structure respectively. The diffraction peaks observed at $2\theta = 37°$, 42.8°, 62.3° and 74.4° correspond to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes in the cubic structure of Mo_2N, and at $2\theta = 38°$, 43.7°, 54.6°, 63.6° correspond to (0 1 1), (1 0 1), (0 2 1) and (1 2 1) planes of CrN.

Both Mo_2N and CrN diffraction peaks appeared in the Mo_2N/CrN multilayer coatings, indicating that the multilayer coatings are in the crystalline structure. The relative intensity of the Mo_2N diffraction peaks in compare to the CrN one is consistent with the sub-layer thicknesses. There was a small shift to the higher angle of the Mo_2N diffraction peaks in the multilayer compared to the Mo_2N monolayer, the lattice parameter decreased from 0.423 nm in Mo_2N monolayer to 0.421 nm at 1.30 μm and 0.422 nm for 1.54 μm multilayer thicknesses. It may be attributed to the decrease (relax) of the residual stresses [12] due to the interfaces between Mo_2N and CrN phases. In multilayer coatings, when the thickness of the period increase up to 220 nm a small shift of the Mo_2N (1 1 1) diffraction peak at low angle, the lattice parameter of Mo_2N increase to a = 0.422 nm. It could indicate an increase of the residual stress, which is in good agreement with the measurements of the residual stress (Section 2). Stöber et al., have reported the shift in the peaks (1 1 1) of γ-Mo_2N cubic phase at low angle as a function of the nitrogen partial pressure [13]. Gilewicz et al., have deposited Mo_2N and CrN phase in the cubic face center with similar lattice parameter, 0.4163 nm (Mo_2N) and 0.4140 nm (CrN) by cathodic arc evaporation, to form the multilayer Mo_2N/CrN coating with small interlayer stress [7].

Zhang et al., reported, the X-ray diffraction result of MoN_x/SiN_x demonstrated, only Mo_2N phase of multilayer coatings was composed and the decrease of stress is due of the disappearance of coherent growth in the multilayer [14].

3.2. Residual stress

The residual stress in all coatings was evaluated by the modified Stoney equation [15,16]:

$$\sigma = \frac{E_s}{6(1-v_s)} \frac{h_s^2}{h_f} \left(\frac{1}{R}\right)$$

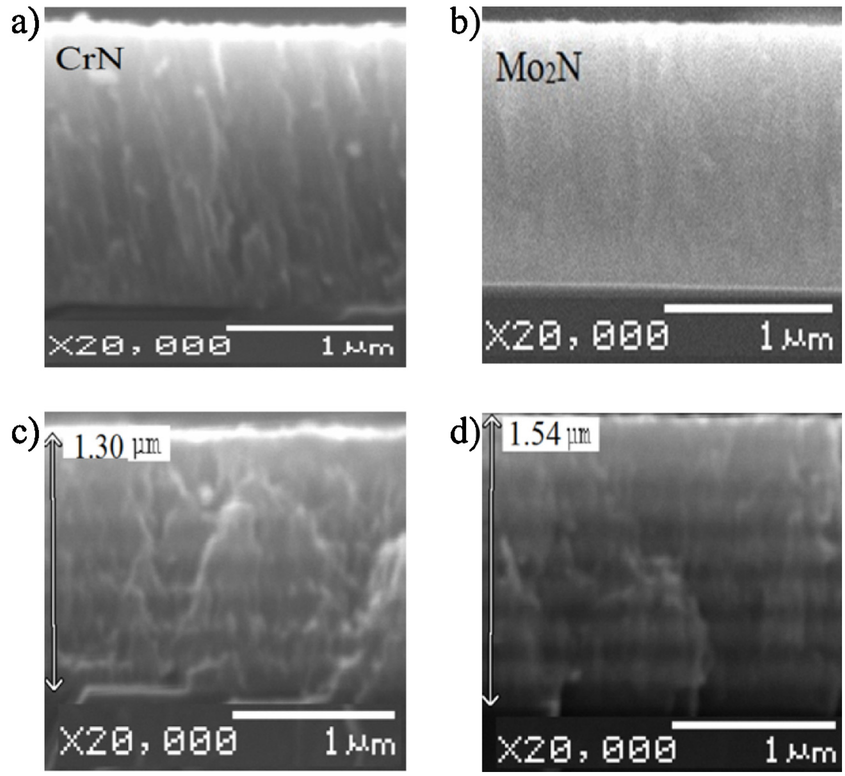

Fig. 2. SEM Cross-section images of individual and multilayer Mo_2N/CrN with different bi-layer thickness.

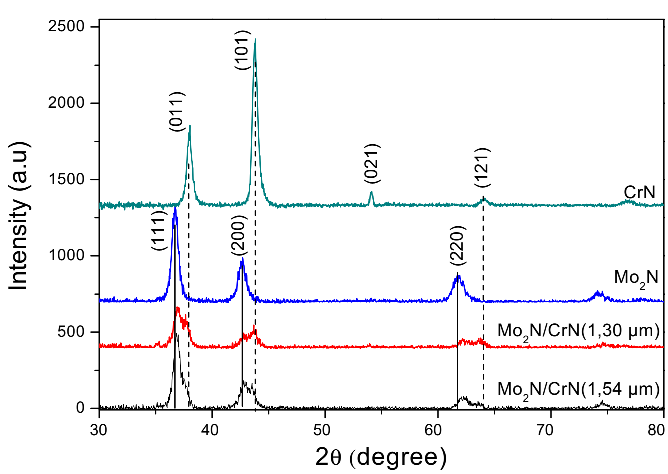

Fig. 3. XRD patterns for Mo_2N, CrN layers and Mo_2N/CrN on Si substrate with different thickness: 1.30 μm and 1.54 μmat working pressure 5×10^{-3} mbar.

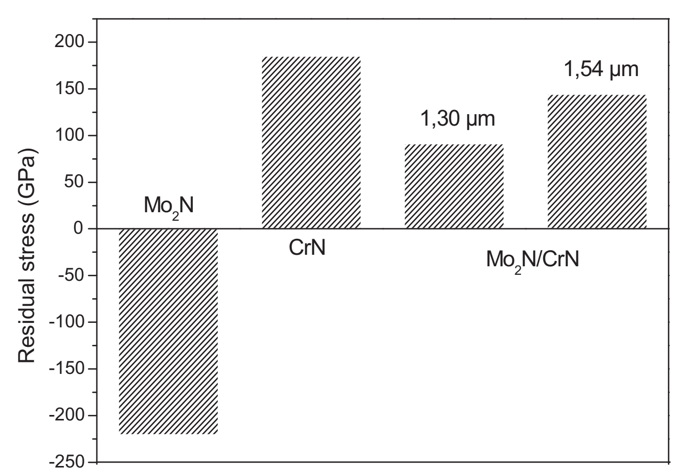

Fig. 4. Residual film stresses of Mo_2N, CrN and Mo_2N/CrN as a function of the bi-layer thickness.

With E_s the Young's modulus of the substrate (130 GPa), ν_s the Poisson's ratio (0.28) and h_s the thickness of the substrate, h_f the thickness of the film, R the mean radius of the strain curvature. The orthogonal radius of curvature R_1 and R_2 were measured by "Gwyddion" on the image of the substrate strain (subtraction of the images before and after coating obtained by optical profilometer [16]). The residual stresses of the four coating are presented in Fig. 4.

The Mo_2N monolayer presents the highest absolute stress value at 220 MPa where the CrN reach 190 MPa, but Mo_2N is compressive while CrN is tensile. A tensile stress into the multilayer coatings is observed due to the first layer deposited Cr and CrN respectively, and as the thickness of the period film increases the tensile stress increase. When the period thickness increase, the compressive stress of Mo_2N coating relaxes and affects the tensile stress of the multilayer coating who also increase. The difference of the crystallographic structure between Mo_2N (cubic) and CrN (orthorhombic) can induce an increase of the tensile residual stress. The residual stress of multilayer coatings is less than the monolayer Mo_2N and CrN film could be indicative of stress relief as defects migrate to interfaces.

3.3. *Nanoindentation*

The hardness and elastic modulus are measured by nanoindentation at 100–230 nm depth to avoid influence of the sub-layer and the interface in multilayer coatings. Fig. 5 shows the loading and unloading curves of multilayer coatings with different period of 186 nm and 220 nm. In multilayer coating of 1.30 μm thickness, the maximum penetration is observed with a large load-unload curve, which indicates that plastic deformation is produced after

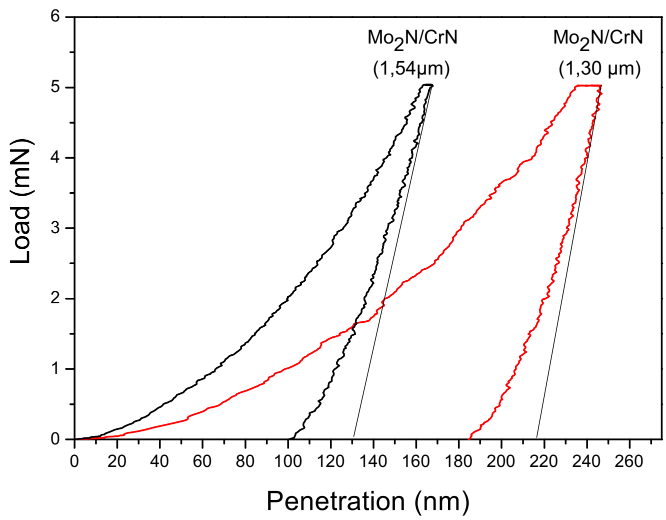

Fig. 5. Load-displacement for multilayer coatings Mo_2N/CrNat different period thickness.

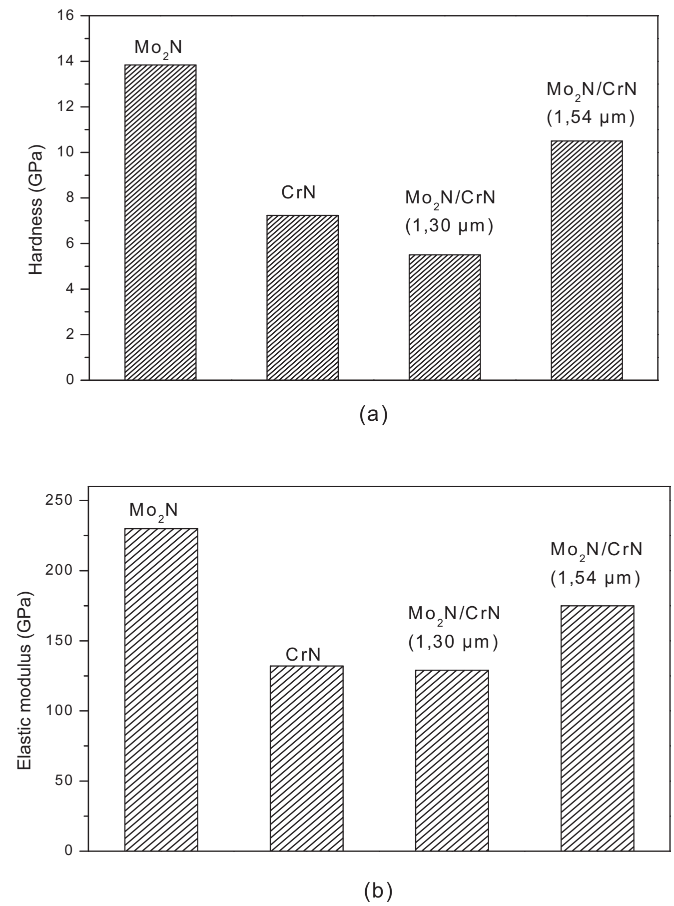

Fig. 6. Hardness (a) and elastic modulus (b) for different layers Mo_2N, CrN and multilayer Mo_2N/CrN as a function a period thickness.

indentation due to the effect of the penetration of the indenter across the interface and the sub-layer CrN. The coating of 1.54 µm thickness exhibits a lower indenter penetration than the 1.30 µm multilayer thickness, indicating that the film was most resilient to elastic-plastic deformation. In general, high compressive stresses lead to harder films, whereas tensile stresses lead to softer films. We observe that, the elastic modulus qualitatively follows the evolution of the hardness (Fig. 6).

See to the tensile residual stress of multilayer coatings, the results for hardness and elastic modulus are different to those expected. It was found that hardness and elastic modulus increase with tensile stress in multilayer films. We can explain this by the first layer deposited Cr and CrN caused the tensile stress and the upper layer of Mo_2N induces an increase in the hardness and elastic modulus. Pharr et al., have reported that decreases in the experimentally hardness and modulus with increasing stress in the nanoindentation experiments in aluminum alloy 8009 and are not real, because the pileup in nanoindentation measurements gives rise to an apparent but unreal change in hardness and elastic modulus [17]. Koshy et al., have reported that the annealing of Mo_2N/CrN films induce a drop in hardness which could be indicative of stress relief as defects migrate to free surfaces or interfaces [18].

The Mo_2N coating showed higher hardness and elastic modulus of about 14 GPa and 230 GPa than the CrN coating with 7 GPa and 132 GPa respectively. The reduce of the hardness and elastic modulus of CrN coating can be explain by the columnar structure, The columnar grain boundaries often act as sites for crack initiation resulting in failure of the coatings [2]. The studies by Kot et al. [19] on Cr/CrN multilayer coatings deposited by a pulsed Nd:YAG laser, indicate that the decreased hardness can be explained by the loss of the multilayer behavior, i.e. the lack of clear interfaces between particular layers. The obtained value of the hardness and elastic modulus in multilayer coatings, H (6–10 GPa) and E (129–175 GPa) increases with increasing periodic thickness of the layers. Yin et al., have reported that the residual stress is crucial to adhesion of multilayered coatings, adhesion of the TiN/CrN interface increases almost linearly with the residual stress [20].

4. Conclusion

The multilayer Mo_2N/CrN thin films have been successfully prepared by RF magnetron sputtering at room temperature. Molybdenum nitride and chromium nitride layers are well crystallized, where their internal hetero-interfaces and corresponding residual stress have been influencing their hardness and elastic modulus. Multilayered Mo_2N/CrN was found to have superior properties than CrN in orthorombic structure and less property than Mo_2N film.

We have correlated and studied the effect of the bi-layer thickness of Mo_2N/CrN films on the mechanical and micro structural properties. Increasing the thickness of the period in multilayer induce an increase of the tensile stress measurement in multilayer coatings, and is well agree with the shift of the XRD diffraction peak (1 1 1) of Mo_2N. The multilayer with lower period thickness has lower residual stresses, elastic modulus and hardness.

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