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Nanoindentation of chromium zigzag thin films sputter deposited

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Chromium thin films exhibiting a columnar microstructure were prepared by dc magnetron sputtering. The glancing angle deposition technique (GLAD) combined with the periodical changing of the incidence flux angle from α to $-\alpha$ was used to sculpt chromium thin films following a zigzag microstructure. The zigzag microstructure was systematically modified varying the flux angle α from 0 to 50° and the half-period thickness λ from 50 to 1000 nm. The changes in the microstructure were correlated with the evolution of the film's hardness and reduced Young's modulus obtained by nanoindentation. The drop of the film's hardness from $H = 10$ to 1.4 GPa and the reduced Young's modulus from $E_r = 245$ to 91 GPa was noted with increasing flux angle α and half-period thickness λ . In agreement with the Hall-Petch effect, the diminution of the half-period thickness of chromium zigzag thin films led to an improvement of the nanohardness of chromium thin films deposited at the normal incidence up to 160%. The surface roughness and film's porosity depend strongly on the microstructure of the zigzag thin films. The influence of these parameters on the indentation of the zigzag thin films was also discussed. It was shown, that the Young's modulus depends on the films porosity. Correcting the films porosity using the mixing rule, the contribution of the flux angle and the number of layers could be easily demonstrated. For the small half-period thicknesses, values of Young's modulus of the coatings tend to be that of the bulk chromium.

Keywords: Nanoindentation; Chromium; Zigzag; GLAD

1. Introduction

Thin films deposited at low pressure and low substrate temperature exhibit a typical columnar microstructure [1]. If the Glancing Angle Deposition (GLAD) technique, firstly published by Knorr and Hoffman [2] and later by others [3–5], is combined to the special substrate motion the Sculptured Thin Films (STF) are obtained [6]. Such coatings exhibit a physical behaviour different to the normally deposited ones. The zigzag coatings are obtained by periodical changing of the direction of the incident flux from α to $-\alpha$. Flux angle α and the column angle β are measured from the substrate normal. It was shown that the modification of

the microstructure by the GLAD technique is an easy and original way to extend the film properties. The influence of the flux angle on the electrical properties and some mechanical properties were published previously [7,8].

In this article, we report on the correlation between the microstructure of chromium zigzag thin films deposited at different flux angles with different single period thicknesses and the nanohardness, and reduced Young's modulus of these coatings. The film microstructure (column diameter, column angle) was examined from the film's cross section observation using Scanning Electron Microscopy (SEM). The decrease of the nanohardness and reduced Young's modulus with the flux angle and the number of periods is discussed taking into account the combined influence of the films porosity and the real film's geometry. The change of behaviours for the flux angles included between 10 and 30° is often noted.

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2. Experimental details

Chromium coatings with zigzag microstructures were sputter deposited from a chromium target of 5 cm diameter (purity 99.6%) with an argon pressure $P_{Ar}=0.6$ Pa and at room temperature on Si(100) substrates. The base pressure was lower than 10^{-5} Pa before introducing the argon to set up the working pressure. The target was dc powered with a constant current density $J=42$ Am⁻². A 11-position substrate holder was made to vary the flux angle α from -50 to 50° with a target-to-substrate holder distance fixed at 6.5 cm. The flux angle α was measured from the centre of the target to the substrate normal in the rotation axis of the substrate's surface. Monitoring the target potential [9] and considering the different film's geometry, the deposition time was adjusted to keep a film thickness close to 1 μ m. Si(100) substrates were ultrasonically cleaned in acetone and alcohol before introducing them into the reactor. SEM observations of the film's cross section were made to determine the column tilt angle and the column diameter. The film's porosity was determined as the difference of the film and the bulk material density divided by the bulk density. The film density was obtained from the weight and the dimensions of the film. The mechanical properties were performed using CSM nanoindenter with a Berkovich indenter in dynamic mode. The film's nanohardness and reduced Young's modulus were determined for each sample as the mean values of 15 series of measurements.

3. Results and discussion

Since the chromium thin films are prepared at low pressure and low substrate temperature, the cross sections of the films deposited on Si(100) exhibit a typical columnar microstructure (Fig. 1). It is in agreement with the Thornton's structural zone model [1]. An increasing flux angle α and a large number of periods n both influence the films microstructure. It was previously shown [7] that for chromium thin films the column tilt angle β is lower than the flux angle α fitting the well known tangent rule [3,4,10,11]. Since the film thickness was kept constant close to 1 μ m, one period thickness decreases with the number of periods. In addition, the deposition rate is nearly constant, and then, one layer deposition time decreases too. For the film composed of 10 periods 100 nm thick one layer deposition time is too short to allow the formation of the columns and instead of the typical columnar microstructure, the microstructure like "curly hair" is formed [8].

The flux angle α and the number of periods n both influence the porosity of chromium zigzag multilayers (Table 1). In agreement with literature [12,13], for $\alpha > 20^\circ$, the porosity increases with the flux angle regardless the number of periods. But up to a flux angle

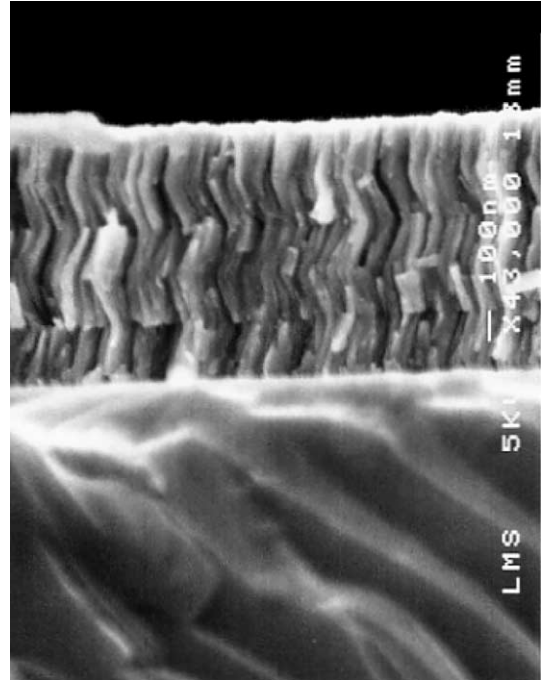


Fig. 1. SEM observations of the film's cross section composed of 3 periods deposited with the flux angle $\alpha=30^\circ$.

of 20° , the porosity of the chromium zigzag thin films remains nearly constant. This latter could be explained by the increasing influence of the misoriented growth of the films for the small flux angles. This misoriented growth was also observed on ballistic simulation of the film growth by Leamy and Dirks [14]. On the other hand, any significant influence of the number of periods n on the porosity of chromium zigzag multilayers is not noticed. Therefore one can conclude that after the first stages of growth, the columns in the chromium coatings grow regularly. They are identically spaced and the difference of the column's diameter along the film thickness is not significant.

Nanohardness and reduced Young's modulus, determined by nanoindentation, are not constant with the penetration depth. Usually one can distinguish three zones. In the case of chromium zigzag multilayers 1 μ m thick, for the indentation depth h up to 40 nm, there is a strong influence of the film surface (roughness, chemical states of the surface, ...). Taking into account the mean RMS roughness (between 5 and 12 nm) and applying the rule presented by Delobelle and Qasmi [15], ($\Delta E/E = 0.346(\text{RMS}/h)^{0.64}$), the standard deviation of the reduced Young's modulus caused by the roughness at an indentation depth of 50 nm ranges between 7 and 13% for different thin films. For h included between 40 and 90 nm one can consider that there is an indentation of the film, because the influence of the surface and the substrate is negligible. For $h > 90$ nm, the influence of the substrate becomes important. In order to avoid this influence and to compare the coatings, a penetration depth was chosen to fulfil the rule of maximal

Table 1

Film porosity as a function of the flux angle α and the number of periods n

α (°)	$n=1$	$n=3$	$n=5$	$n=10$
0	10.4 ± 2.6	18.3 ± 4.6	12.7 ± 3.2	14.9 ± 3.7
10	8.8 ± 2.2	11.9 ± 3.0	12.3 ± 3.1	7.5 ± 1.9
20	6.3 ± 1.6	7.6 ± 1.9	16.2 ± 4.0	20.4 ± 5.1
30	10.4 ± 2.6	14.9 ± 3.7	11.1 ± 2.8	18.1 ± 4.5
40	31.5 ± 7.9	24.1 ± 6.0	20.9 ± 5.2	27.7 ± 6.9
50	50 ± 12.5	33.3 ± 8.3	34 ± 8.5	25.1 ± 6.3

penetration depth $h_{\max} < 0.1 d$ (d =film thickness) at 50 nm [16], ($h/d=5\%$). The reduced Young's modulus is first influenced by the surface (up to 40 nm), then it remains nearly constant and finally it approaches the substrate Young's modulus value. The nanohardness decreases up to 40 nm mainly due to the roughness and the oxide layer on the surface. Afterwards, it increases due to the combined effect of the hardening of the film during the deformation and the influence of the substrate. For an indentation depth higher than 90 nm, the influence of the substrate predominates. This corresponds to the slight change of the slope of the nanohardness as a function of the indentation depth.

Since the zigzag coatings exhibit anisotropic behaviours [17], the Poisson's ratio is unknown in both perpendicular directions. Therefore the reduced Young's modulus (defined as $E_r = E/(1 - \nu^2)$) is used to compare the coatings.

In Fig. 2a, one can see that the nanohardness decreases strongly from 10 to 1.4 GPa with the increasing flux angle and decreasing number of periods. Since the total film thickness was kept constant close to 1 μm , one period thickness decreases with the number of periods. Therefore, in agreement with the Hall and Petch effect [18], the nanohardness of chromium zigzag thin films increases with decreasing one period thickness. In addition, as previously shown for single oriented chromium coatings [7] and for a zigzag microstructure as well, a much more porous structure is obtained as the flux angle α is increased. Such a porous structure becomes significant especially for α higher than 20–30°. As a result, films deposited at high flux angles ($\alpha > 30^\circ$) are composed of inclined columns separated by important voids. These ones reduced the amount of probed matter during the indentation test leading to the decrease of hardness.

The same behaviour is obtained for the reduced Young's modulus (Fig. 2b). This latter drops from 245 to 91 GPa with the flux angle. Inversely, it is enhanced with the number of periods. The maximal value of the film's reduced Young's modulus ($E_{r_{\text{film}}} = 245$ GPa), obtained for the film composed of 5 periods deposited with the normal incidence flux, is much lower than that of the bulk material value ($E_{r_{\text{bulk}}} = 292$ GPa).

At first, one can suppose that this important decrease of nanohardness and reduced Young's modulus with the flux angle is directly linked to the much more porous structure of the films [19]. Therefore one can suggest to extract the contribution of the porosity applying the mixing rule. This

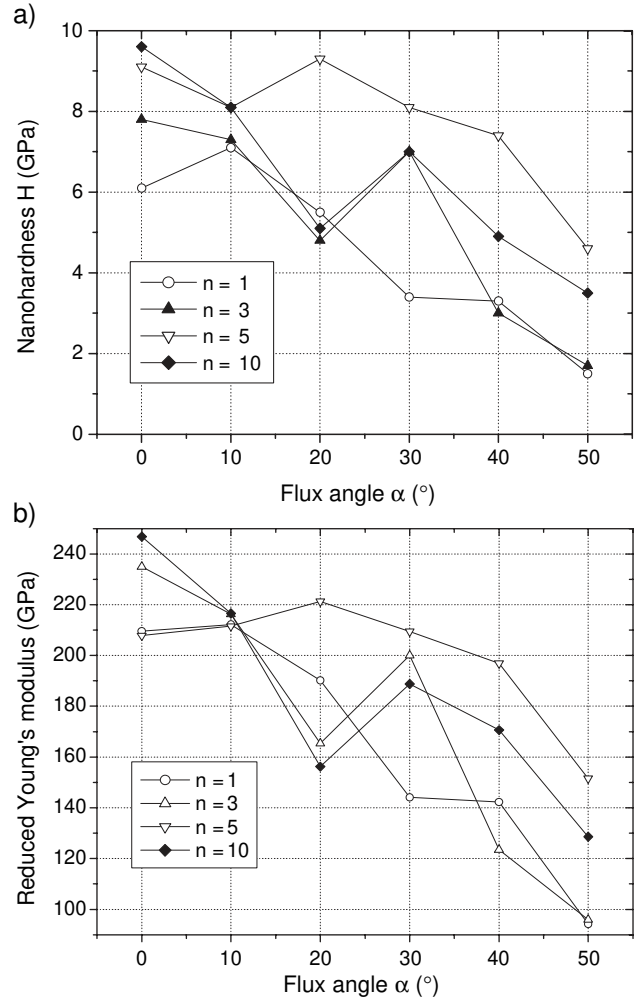


Fig. 2. Influence of the flux angle α and the number of periods on the mean value of the nanohardness H (a) and reduced Young's modulus E_r (b) measured at a penetration depth of 50 nm.

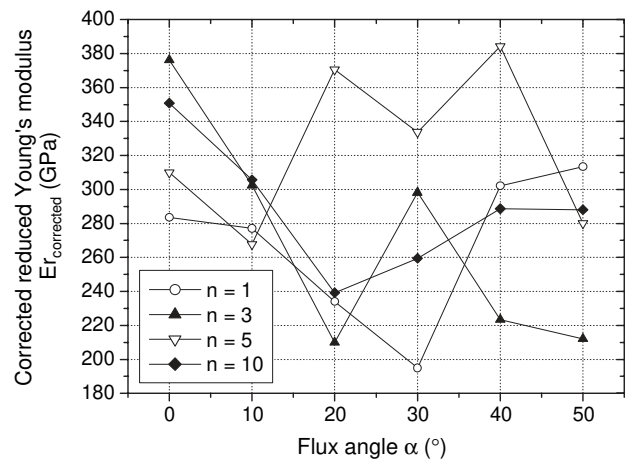


Fig. 3. Corrected reduced Young's modulus $E_{r_{\text{corrected}}}$ as a function of the flux angle and the number of layers after the extraction of the influence of the porosity using the "mixing rule".

latter was used as the first approach, and is defined as the following relationship [20]:

$$E_{\text{corrected}} = \frac{E_r}{(1 - f^{2/3})^{1.21}}$$

f is the volumetric fraction. If the corrected reduced Young's modulus is plotted as a function of the flux angle (Fig. 3), one can see that the influence of the film porosity is the most important parameter influencing the reduced Young's modulus. Taking into account an experimental error due to the influence of the roughness (12%), the values close to that of the bulk chromium (292 ± 35 GPa) are obtained. Therefore one can say that the choice of the mixing rule is appropriate to extract the influence of the film's porosity on the reduced Young's modulus. Nevertheless, the influence of the flux angle on the reduced Young's modulus still remains. One can distinguish that except the films composed of 5 periods, whose porosity measurement seems to be modified, the evolution of the corrected reduced Young's modulus as the function of the flux angle can be noted. There is a decrease of the reduced Young's modulus values vs. the flux angle with a minimum located between $\alpha=10$ and 30° . Young's modulus is significantly influenced also by other factors. The film's geometry is one of the most important parameters. Influence of the film geometry can be easily explained using a simple mechanical approach. If the column angle β is kept constant and the single layer thickness (λ) is increased or if the single layer thickness λ is kept constant and the column angle is changed, the force F acts on the longer distance and creates a stronger bending moment. Consequently, the displacement of the top of the zigzag is more important. It is well known that the Young's modulus is inversely proportional to the displacement. Therefore, in agreement with experimental values, the reduced Young's modulus decreases with the flux angle and the single layer (one period) thickness.

Even if the hardness is a plastic parameter, similar conclusion can be drawn, since the higher displacement corresponds to the softer coatings. The experimental results correlate well with the proposed mechanical approach.

4. Conclusion

Varying the flux angle α and the number of periods n , chromium thin films with different columnar zigzag

microstructures are obtained. The film porosity is influenced mainly by the flux angle α . It is nearly constant up to 20° then it increases with the flux angle. The film nanohardness measured at 50 nm is strongly influenced by the flux angle and the number of periods. While nanohardness increases with the number of periods it decreases with the flux angle. Nearly the same behaviour is obtained for the reduced Young's modulus. It was shown that the film porosity is an important parameter determining the mechanical properties of the chromium zigzag coatings. In addition, the zigzag microstructure has also a very important influence on the mechanical properties of sculptured thin films.

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