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Investigation of vanadium and nitride alloys thin layers deposited by PVD

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Abstract. In this work we present the technique of magnetron vapor deposition and the effect of several deposition parameters on the structural and morphological properties of prepared thin films. It was noted that the deposition time has an effect on the crystallinity, mechanical properties such as residual stress, roughness surface and the layer composition from target products. Studies were carried out on layers of vanadium (V) and the nitride vanadium (VN).
Keywords. PVD, VN, electrical resistivity, roughness, residual stress.

1 Introduction

Making materials in the thin film presents a main interest in very varied application, since the last decade we observe an increasing interest for studying surfaces for their essential role to exert a decisive influence on diverse characteristics as well as corrosion, catalyses, friction (wear, lubrication...), adherence, sintering, [1-5].

Alloys containing chromium and nitrogen present varied properties which makes a particularly interesting for mechanical, optical and electrically applications. CrN has been gaining a great importance due to its superior corrosion and wear resistance, friction behavior and low internal stress[4,5]. However, there are an increasing number of applications. Others authors[6] studied the efficiency of CrV and Cr coatings in reducing cutting edge wear of steel milling tools. In a first vision the objective in our present study is to analyze the effects of the deposition conditions such as the deposition duration, the rate of different alloys constituting the V and VN in physical and mechanical properties.

2 Sample preparation

Thin layers of vanadium and nitride vanadium are filed on silicon platelets, using a magnetron sputtering mode DC from two targets of high purity. The backings were mounted on a continuously

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rotating planetary holder inside the vacuum chamber (fig. 1). The atmosphere was chosen in order to produce a V and VN layer respectively. Thin film layers are deposited onto samples of amorphous silicon, with different deposition duration. The film deposition was carried out by a dual Radio frequency (RF) magnetron sputtering system (NORDIKO type 3500–13.56 MHz) from targets of high purity (99.999%) with 10 cm of diameters. Prior to deposition, the samples were polished and then cleaned with acetone in an ultrasonic container for 15 min. Subsequently, they were rinsed in deionized water, dried and stored in desiccators prior to coating deposition. The targets were sputter cleaned for 5 min. Then the samples were sputter-etched with argon ions (10 mbar, applied bias voltage -900 V) for approximately 10 min to remove surface oxide and pollution. All of the two targets were sputtered using RF power. During deposition, the substrate temperature was 150 °C. The pressure in the deposition chamber was 10^{-6} mbar. The distance between the target and surface backing was 10 cm. Moreover, the samples were mounted on a continuously rotating planetary holder inside the vacuum chamber. The composition of the as-deposited coatings was measured by energy dispersive analysis of X-rays (EDX), which is attached to a scanning electron microscope, at 10 keV and the INCA quantitative analysis software.

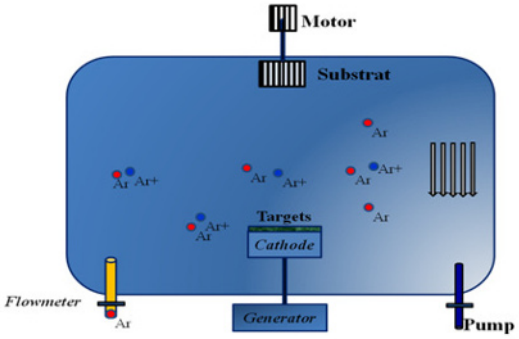

Fig.1. Experimental set-up used to deposited V or VN thin layers

3 Results and discussion

3.1 Vanadium Layer

3.1.1 Structural properties

The observation of the morphological surface is realized by the SE microscope on the cross section gives the fig. 2 for a Vanadium layer. In the fig. 3 is reported the thickness layer the evolution versus the duration deposition. We notes that this layer increases linearly which permits to achieve an average speed deposition in the order of 10.8 nm.min^{-1}.

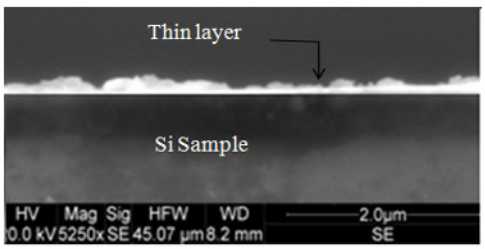

Fig. 2. Cross section by SE microscope of the vanadium layer

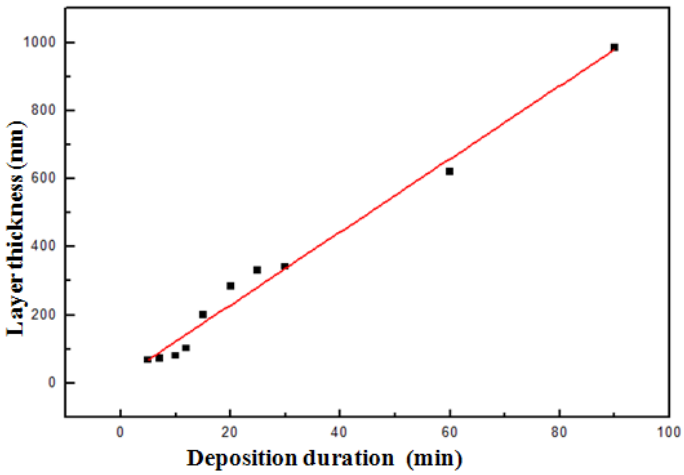

Fig.3. Evolution of the layer thickness with the deposition duration

The fig. 4 gives the surface AFM photos in three dimensional of the deposited vanadium thin layer. What presents a granular structure was their grains size increase with the deposition duration and this can be traduced by the formation of the Vanadium layer in a first step with dome particle and in a second step with grains in a needles type whose diameter and maximal haughtiness respectively in the order of 38 nm and 8 nm, and however presents an increase of its surface roughness with deposition duration.

Moreover the surface arithmetic roughness (Ra) varies with the deposition duration in which their values for the different samples is given in the fig. 5 and who values vary between 0.53 and 3.7 nm.

The samples EDX spectral, Obtained with a tension of 25 kV are given in the fig. 6 where we notes the presence of two characteristics picks of the Vanadium at 4.945 and 4.952 kev whose intensities increases with the deposition duration.

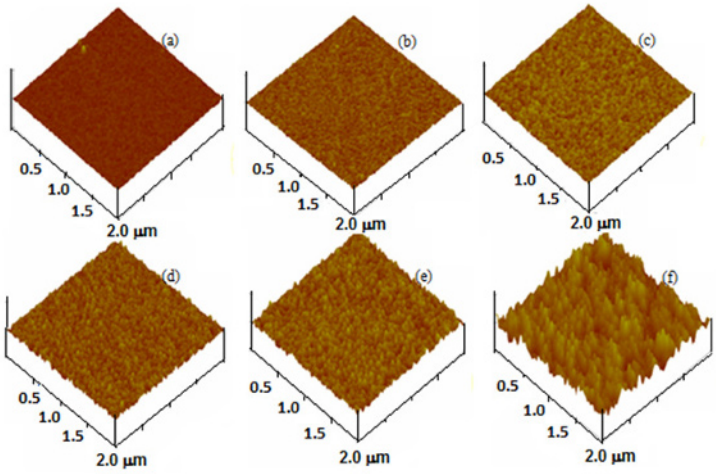

Fig.4. The surface AFM photos in three dimensional of the deposited vanadium thin layer carry out to a tapping mod for various deposition duration: (a) 5min, (b) 7min, (c) 12min

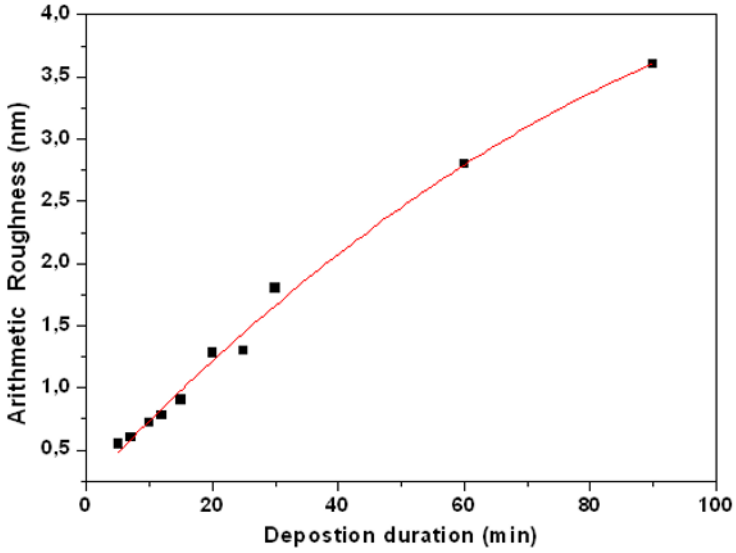

Fig. 5. Variation of the surface roughness with the deposition duration

On top of that one can observes the picks of oxygen and silicon that can give the material atomic percentage constituting the layer which its values are reported in the table 1.

One remarks host presence of the carbon in our films, this component is an impurity probably due to the poor quality of the vacuum pump oil, we supposes that its affects in the films properties are globally homogeneous and physical properties changes are due to variation of its thickness films.

Table 1. Chemical composition of the deposited vanadium layer

Component	atomic % (5min)	atomic % (10min)	atomic % (30min)	atomic % (90min)
C	3.25	4	12.55	6.43
O	1.7	2.77	12.79	28.29
Si	92.85	88.71	68.75	28.22
V	2.2	4.52	10.91	37.06
Total	100	100	100	100

In order to determine the X-ray diffraction pattern, we used BRUKER AXS D8 ADVANCE spectrometer through the beam length 1.54056 Å of the (CuK_{α}) copper, with a bias voltage 40kV and current 20 mA, by placing the samples that are treated with different depositions durations according to Bragg Brentano ($\theta/2\theta$) geometry.

The obtained XRD patterns are reported in fig. 7, when we note the presence of two Vanadium picks (200) and (110) on $2\theta = 61.8°$ and 41.3°. We remark that all patterns are almost identical unless that present one pick corresponding to the (110) orientation of the V component whose intensity increase progressively. It emerge from this that the deposition duration not affect the final films structure whilst that their thickness are small and when we increases this layer it structure changes.

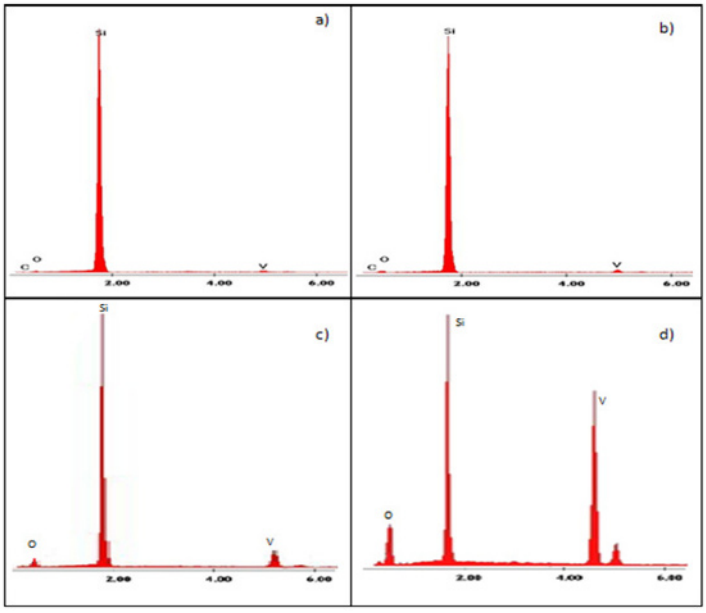

Fig.6. EDS analysis of the deposited vanadium layer with the deposition duration: 5min (a), 7min (b), 30 min (c) et 90 min (d)

The mean crystal size has been (fig.8) calculated using the Debye Scherrer formula. The half pick width is determined from the spectrogram recording a θ-2θ mod and the calculation of the mean size of the formed particle is realized by considering the (110) pick.

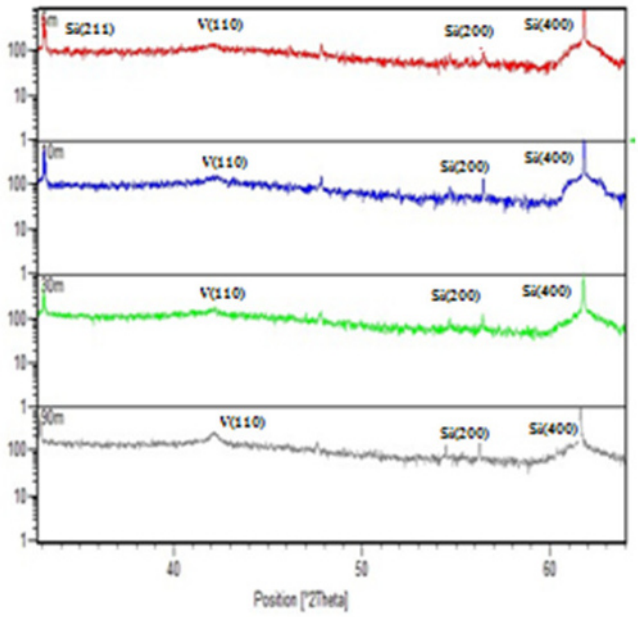

Fig. 7. XDR patterns of the deposited Vanadium thin film: (a) 5min, (b) 10min, (c) 30min, (d) 90min

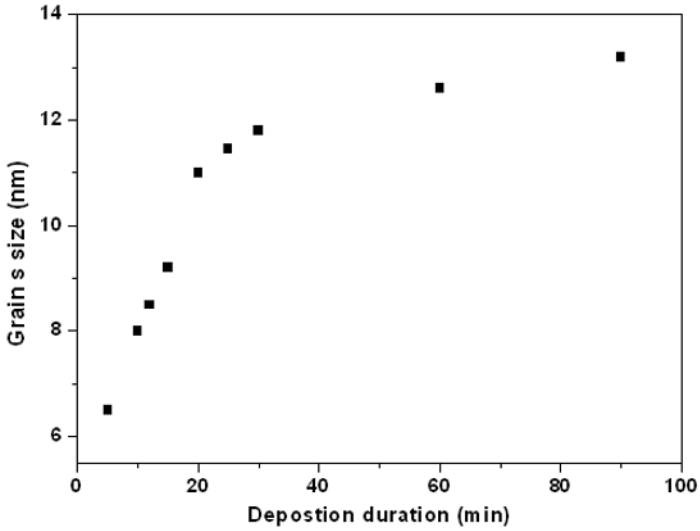

Fig. 8. Grains size evolution versus the deposition duration

3.1.2 Mechanical properties

Like all physical properties, mechanical properties vary with the thickness such as the residual stress, the hardness [7-9,16], the wear resistance [6, 16], the preferential orientation of crystalline plane[13-15]. The influence of the thickness to the layer properties has been studied for several materials such as the AlN [15], BN [16] and the TiN [17]. The effect of the thickness in the residual stress has been studied by Meng [15] and Mckenzie [16] has demonstrated that the residual stress hasn't a homogeneous evolution with its thickness. Besides, Quaeyhaegens and all [17] have demonstrated the thickness effect to the changes in the preferential orientation of the TiN layers.

In this studied case, as it happen the vanadium deposit, we obtain that the residual stress, determined by the Newton method; present a similar evolution with the layer thickness (fig.9).

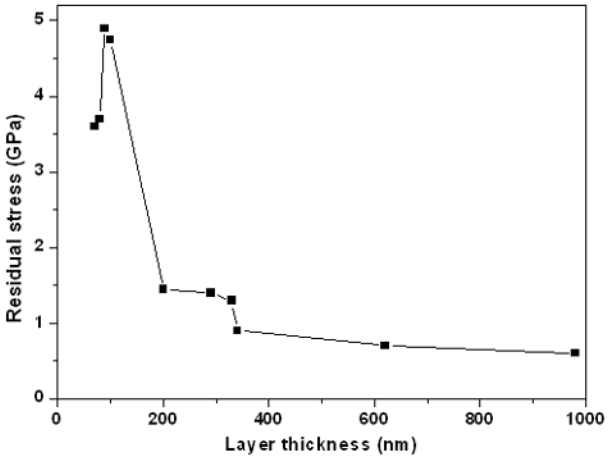

Fig. 9. Variation of the residual stress with the layer thickness

In fact, we remark that the stress isn't constant where the film thickness varies, it increase until about 4.8 GPa for a thickness in order of 80nm and decrease beyond.

The maximal stress can be explained by the various effects that can appear in the course of the increasing layer such as a creation of an internal or external default, crystalline orientation changes, porosity rate.

In the deposition beginning the arrival atoms engender a formation of a smaller particle through a nucleation increases giving a growth with the (200) crystallographic direction and after an increasing of verticals columnar relatively spaced and this process is schematized by Hones [18].

3.1.3 Electrical resistivity

In our work we have measured the electrical resistivity of the vanadium layer with method of the four touches method.

We remark that the electrical resistivity (fig.10) decrease greatly for petites thickness (<300nm), and stabilize for a mean value in the order of 10 $\mu\Omega.cm^{-1}$. This behavior has been observed by Holland [19] for various thin metallic films.

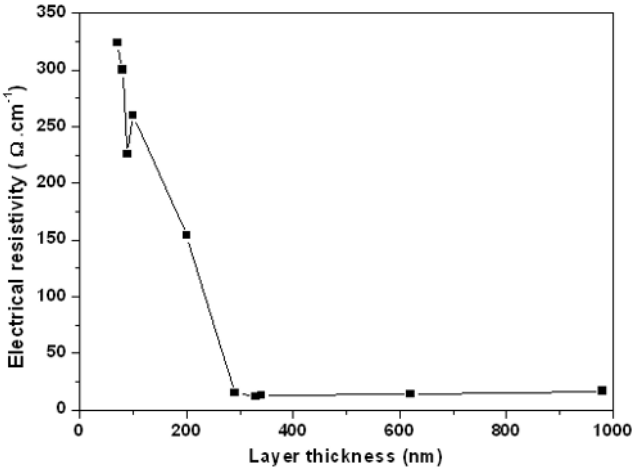

Fig. 10. Variation of the electrical resistivity versus the layer thickness

We can explain this variation by the approach that he vanadium film can be considered as a stocking of any mono-layers infinitely thin whose conductivity increase from the surface toward the film surface. Consequently, this layer can be considered as a resistance associated with parallel disposition; that decrease when the layers number increase.

3.2 Vanadium Nitride layer

In this part we interest to study of the alloys formed by the Vanadium and a Nitride.

3.2.1 Structural analysis

The layers topography of the VN alloys observed by the AFM (fig.11) is globally uniform, it constituted with heaps and minuscule craters repartee inside these lots in the surface layer and this repartition get more and more convinced if the vanadium proportion increase in the considered coating, i.e. when the columnar microstructure is favoured. The measure of the lots mean diameter is about 88 nm also the maximal depth has not pass 30 nm.

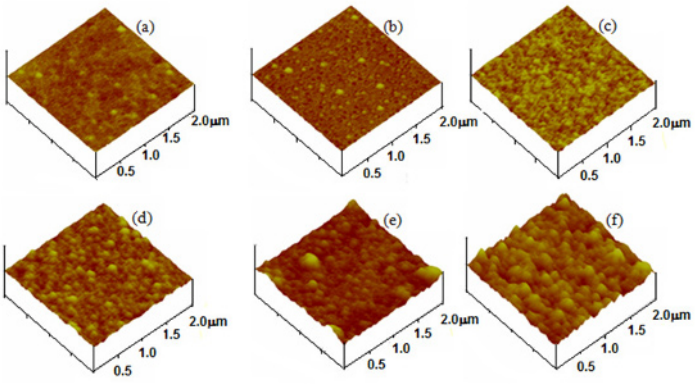

Fig. 11. Three dimensional AFM realized in tapping mod of the deposited VN alloys for different deposition duration: a) 5min, b) 10min, c) 15min, d) 20min, e) 30min, f) 90min

The measure of the surface roughness of the prepared layer is showed in fig. 12, which gives that for a feeble thickness this roughness is almost stable and increase progressively with the deposition duration and believe toward a horizontal asymptote of a values of 1.8 nm characteristic of the massif VN alloys.

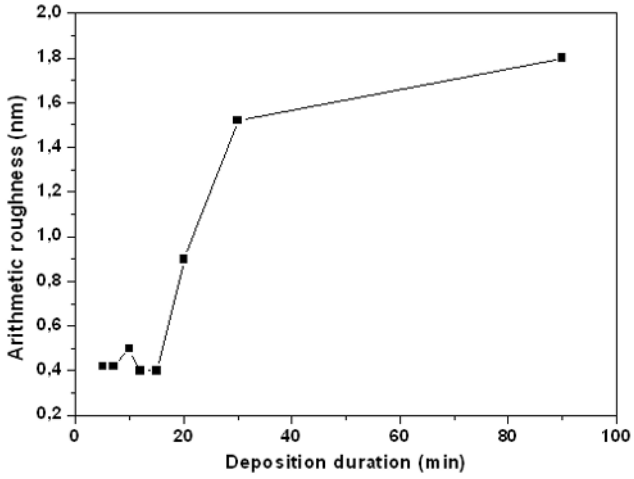

Fig. 12. Variation of the arithmetic roughness of the VN layers with the deposition duration

Patterns obtained by EDS analysis for the VN alloys whatever theirs vanadium content are summarized in fig. 13, which give elements constituting the coatings. In fact, we observe one nitrogen pick in 0,392 keV and two vanadium picks $K_{\alpha 1}$ and $K_{\alpha 2}$ respectively in 4.945 keV and in 4.952 keV.

We remark that if the deposition duration increases, the vanadium peak increases too, that can be explained by an increasing of the pulverization rate of the vanadium target and thus a very important quantity of the Vanadium in the layer.

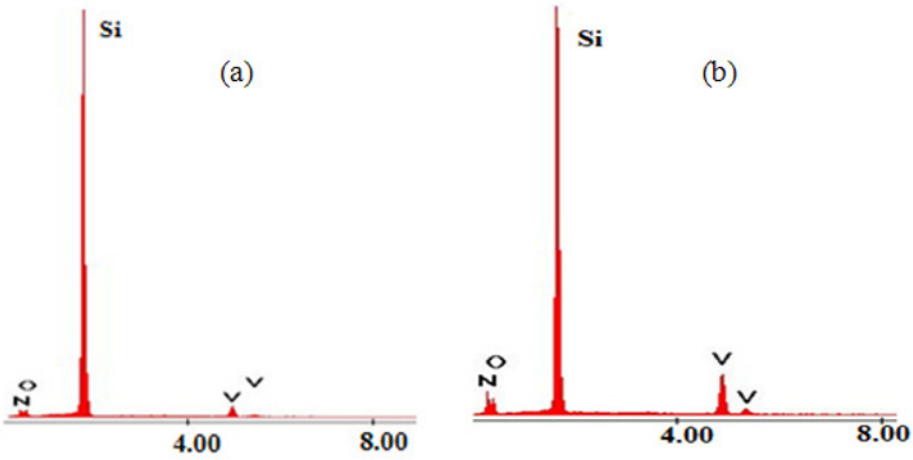

Fig. 13. EDS analysis of the VN layer with the deposition duration: a) 30 min and b) 90 min

The analysis of picks constituting the patterns gives the concentration of each chosen element and permits to obtain their atomic percentage. This values percentage are given in the table 2; we note a slight increase in the nitrogen percentage (it passes from 30.7 to 40.21%) i.e the vanadium addition favorite the film stœchiometry and the nitrogen rate brings to that of the vanadium one.

Table 2. Chemical composition of the deposited vanadium nitride alloys layer

Component	atomic % (30min)	atomic % (90min)
N	18.79	26.17
O	7.85	12.55
Si	68.72	49.52
V	4.63	11.75
Total	100	100

In order to obtain informations on the deposition duration effect in the layer structure, we have fixed the nitrogen percentage in the plasma at 25%, a working pressure to 4 µbar we have varied the deposition duration by choosing values 10, 30 and 90mn. From the spectrogram of fig. 14 we remark that by increasing le deposition duration the film acquire a crystallized structure. The (111) pick amplitude increases and its (FWHM) have tendency to increase with the deposition duration and after the crystallite grain size increase too.
Others study realized to the TiN and CrN alloys shows a crystallographic structure with a (111) ; translating a strongly residual stresses within the layer [20].

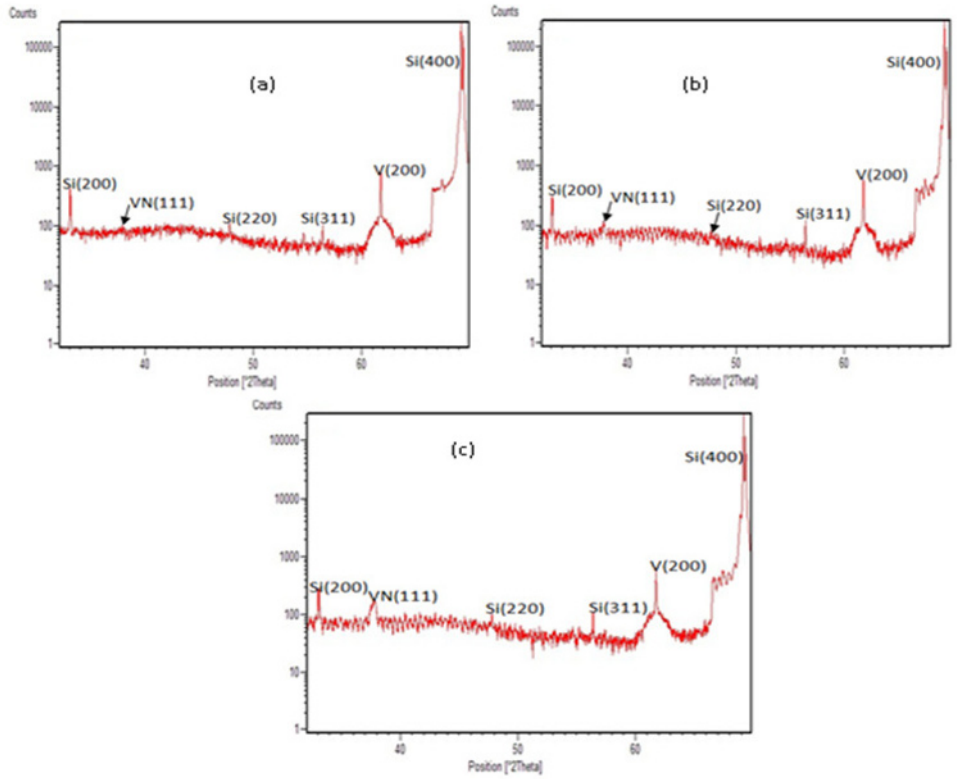

Fig. 14. XRD patterns of the VN alloys for deposition duration equal to: a) 10min, b) 30min and c) 90min

3.2.2 Residual stress

The thickness is one from various parameters that can influence the level of the residual stress of the coatings. The study of the profile of the residual stress gives that this latter is very higher in the beginning of the growth and decrease greatly with the deposition duration and highlights an existence of a maximum of a thin layer of about 88 nm thick.

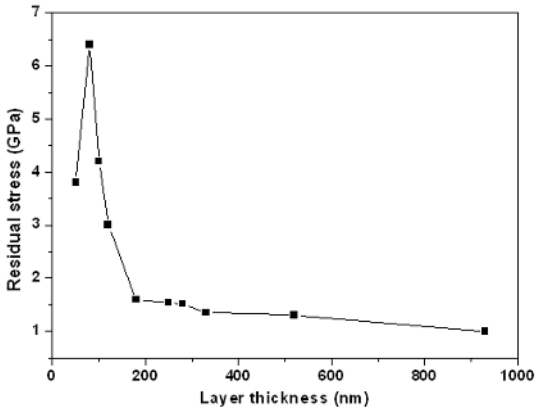

Fig. 15. Variation of the residual stress of the VN alloy versus the layer thickness

Globally this stress is feeble and this can be explained by the amelioration of the cristallinity and textures of these layers how believe toward an equilibrium state and this same conclusion has been observed beforehand during the works of Nouveau and all [21].

4 Conclusion

This preliminary study had been an objective to verify the effect of the deposition conditions on the VN film properties. For this reason we have beginning by study the vanadium layer and after we have realized VN coatings by varying the duration deposition. It demonstrates that the increasing in V or VN layers give a crystalline structure of a very important and regular electrical and mechanical properties. This study is in agreement with others works studying another films like the TiN and CrN alloys.

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