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Temperature effect on the mechanical behaviour of niobium nitride thin films

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Abstract. Niobium nitride is used in a wide range of application due to its mechanical, physical, chemical, electrical and optical properties. The main aim of this paper is to deposit niobium nitride thin films by direct current magnetron sputtering and to characterize them at nanoscale. The films were deposited on silicon Si (100) substrates. Three types of films were deposited by modifying the deposition temperature. In this regard, some of the samples were deposited at room temperature (25 °C), some were deposited when the substrate was preheated at 200 °C, and the rest at substrate temperature of 400 °C. Regarding the topography of the samples, an increase in the average roughness was determined with the increase in deposition temperature. The nanoindentation tests were carried out at temperatures between 20 and 100 °C so that to emphasize the change in hardness and modulus of elasticity in terms of testing temperature. The results pointed out an important influence of both the deposition temperature and testing temperature on the topography, adhesion and mechanical properties of the niobium nitride thin films.

1. Introduction

Transition metal nitrides present, in general, some mechanical, electrical, chemical, physical properties that recommend them for a wide range of application [1-4]. Titanium nitride (TiN), chromium nitride (CrN) and niobium nitride (NbN) are some of the most studied transition metal nitrides. Niobium nitride is characterized by high melting point, high hardness, good superconducting properties, good wear resistance, good stability at high temperatures and so on [5-7].

Niobium nitride is used in application such as wear resistance coatings, diffusion barriers against copper migration, single-photon detectors, superconducting microelectronics applications, Josephson junctions etc. [8-9]. It can be deposited by different techniques such as pulsed laser deposition, reactive magnetron sputtering, cathodic arc evaporation, ion beam assisted deposition, molecular beam epitaxy and all that [10-11].

The deposition conditions such as nitrogen flow rate, deposition temperature, deposition time and so on have a strong influence on the properties of the deposited thin films. This paper is a study concerning the influence of testing temperature on the mechanical properties (hardness and modulus of elasticity) of niobium nitride thin films deposited by direct current (DC) magnetron sputtering at different deposition temperatures.

2. Materials and experimental procedure
Niobium nitride thin films were deposited by direct current (DC) magnetron sputtering on silicon substrates to achieve the purpose of this paper.

2.1. Materials
A high purity niobium target was employed for deposition the niobium nitride thin films. The purity of the target was 99.95 %. The thin films were deposited on Si (100) substrates.

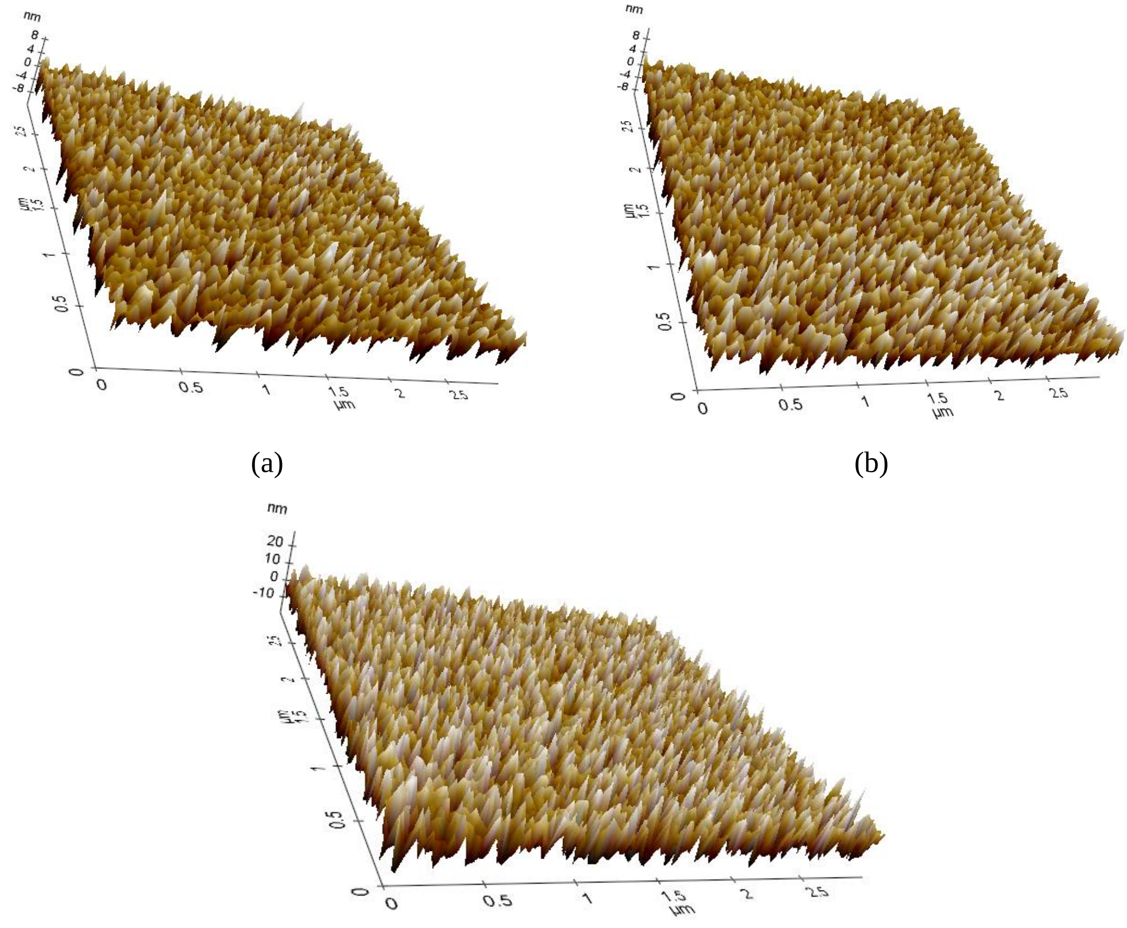
2.2. Experimental procedure
The deposition process took place in a reactive sputtering facility from the Materials Science and Engineering Department, Technical University of Cluj-Napoca. A base pressure of 10^{-7} torr was kept constant inside the deposition chamber. First the silicon substrates were cleaned to remove any possible impurities in an ultrasonic bath with acetone and isopropyl alcohol and blown with compressed air. A mixture of argon and nitrogen was introduced inside the deposition chamber. The pressure and the discharge current were kept constant at 2 mtorr and 350 mA. The argon flow rate and the nitrogen flow rate were 40 $cm^3 \cdot min^{-1}$ and 1.5 $cm^3 \cdot min^{-1}$ respectively. 60 mm were maintained between the niobium target and the silicon substrates. The deposition process ran for 20 minutes. Three types of films were deposited. Some of the samples were deposited at room temperature (25 °C), some were deposited when the substrate was preheated at 200 °C, and the rest were deposited at substrate temperature of 400 °C. The thickness of the deposited niobium nitride thin films was determined using a JEOL 5600LV electron microscope. Its mean value was 0.35 µm.

Once the niobium nitride thin films were deposited, they were characterized at nano scale using a XE 70 atomic force microscope (AFM) from the Micro and Nano Systems Laboratory, Technical University of Cluj-Napoca. All the tests were carried out for a relative humidity of 20 %. The topography of the films was investigated in the non-contact of the AFM using a PPP-NCHR cantilever. The dimensions of this cantilever are: thickness of 4 µm, width of 30 µm, length of 125 µm, resonance frequency of 400 kHz and force constant of 42 $N \cdot m^{-1}$. The tip radius is smaller than 10 nm while its height is 15 µm.

The determination of the mechanical properties was done by nanoindentation tests. These tests were performed using a TD23838 nanoindentor. The stiffness of the nanoindentor is 272 $N \cdot m^{-1}$, its frequency is 50 kHz. The height, thickness and length of the cantilever are 90 µm, 41 µm and 1050 µm respectively. The tip radius is smaller than 25 nm. The tests were carried out at temperatures between 20 and 100 ºC so that to establish the temperature influence on the mechanical characteristics.

3. Results and discussion
First, we investigated the topography of the deposited thin films. This characteristic is strongly influenced by the deposition conditions and the nature of the deposited material. On this line the thin films were scanned in the non-contact mode. The scans were performed on square areas having the dimensions of 2.75x2.75 µm. The tests were done in several areas of each sample to obtain accurate values. The 3D images were obtained using the XEI Image Processing Tools for SPM Data. Figure 1 presents the 3D images of the investigated materials. It can be noticed that the niobium nitride thin films deposited at room temperature have a smoother surface than the thin films deposited on preheated substrates. Instead, the niobium nitride thin films deposited on substrates preheated at 400 ºC are characterized by the rugged surface.

The roughness parameters were determined to support what we noticed on the 3D images. The average roughness, R_a, the root mean square, R_z, the skewness, R_{sk}, and the kurtosis, R_{ku}, are given for the three type of niobium nitride thin films in table 1. If the skewness is an asymmetry indicator, the kurtosis is an indicator of the shape of the distribution's tail. The average roughness increases with the increase in deposition temperature. A small increase of this roughness parameter was determined when the substrate temperature increased from 25 to 200 ºC. Instead, the increase in substrate temperature from 200 to 400 ºC led to the increase in average roughness of about 2.5 times.



(a) (b)

(c)

Figure 1. 3D images of the niobium nitride thin films deposited on silicon substrates at (a) 25 ºC, (b) 200 ºC and (c) 400 ºC.

Table 1. Roughness parameters of the deposited niobium nitride thin films.

Deposition	Roughness parameters			
temperature (ºC)	R_a (nm)	R_z (nm)	R_{sk} (-)	R_{ku} (-)
25	1.9	18.9	0.7	3.9
200	2.1	18.2	0.2	3.0
400	5.2	42.3	-0.1	2.4

Z scan vs. force curves were achieved after each indentation (Figure 2). These curves were further interpreted using the XEI Image Processing Tools for SPM Data. The interpretation was realized using both the Oliver and Pharr method and the Hertzian method. If the first model allows us to determine the hardness, the second one allows us to determine the modulus of elasticity. The main difference between these two models is given by the presence/absence of the plastic deformation. On this regard, the Herztian method assumes that there is only elastic deformation, while the Oliver and Pharr method assumes that the material suffers both elastic and plastic deformation. The interpretation takes into account for both methods the Poisson's ratio specific to the tested material – niobium nitride, in our case. If the Oliver and Pharr does not require any other characteristics, the tip shape and the face angle have to be specified in the Hertzian model.

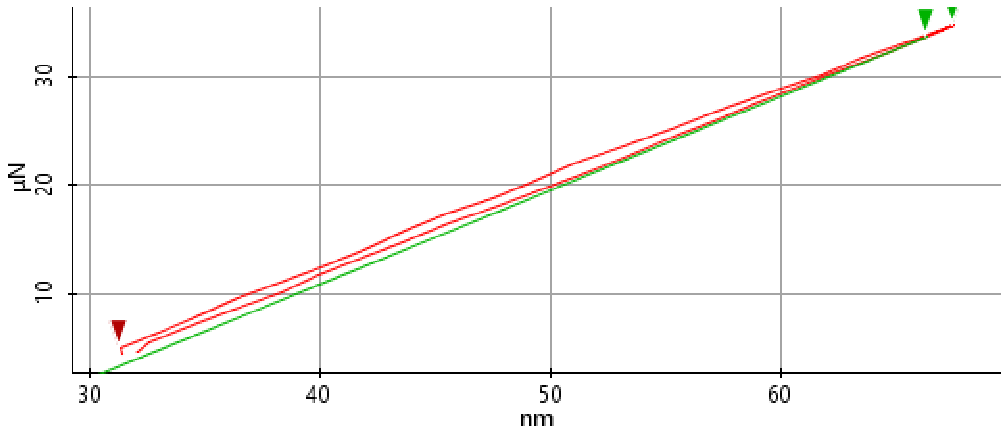


Figure 2. Z scan vs. force curve for a niobium nitride thin film deposited on silicon substrate at room temperature and tested at 20 ºC.

The fluctuation of the modulus of elasticity for the niobium nitride thin films deposited at 25, 200 and 400 ºC and tested at temperatures between 20 and 100 ºC is graphically given in Figure 3. We can affirm that the niobium nitride thin films deposited on silicon substrates at room temperature are characterized by the highest value of the modulus of elasticity regardless of the testing temperature. When varying the deposition temperature, the decrease in this mechanical property ranged between 10 % (when the films were tested at 100 ºC) and 15 % (when the films were tested at 20 ºC). If the modulus of elasticity of niobium nitride deposited at 25 and 200 ºC decreased with about 22 % when the testing temperature increased from 20 to 100 ºC, the modulus of elasticity of niobium nitride deposited at 400 ºC decreased less (about 17 %). When the tests were performed at 20 ºC, the modulus of elasticity ranged between 117.6 GPa (for the films deposited on silicon substrates at 400 ºC) and 138.8 GPa (for the films deposited on silicon substrates at room temperature).

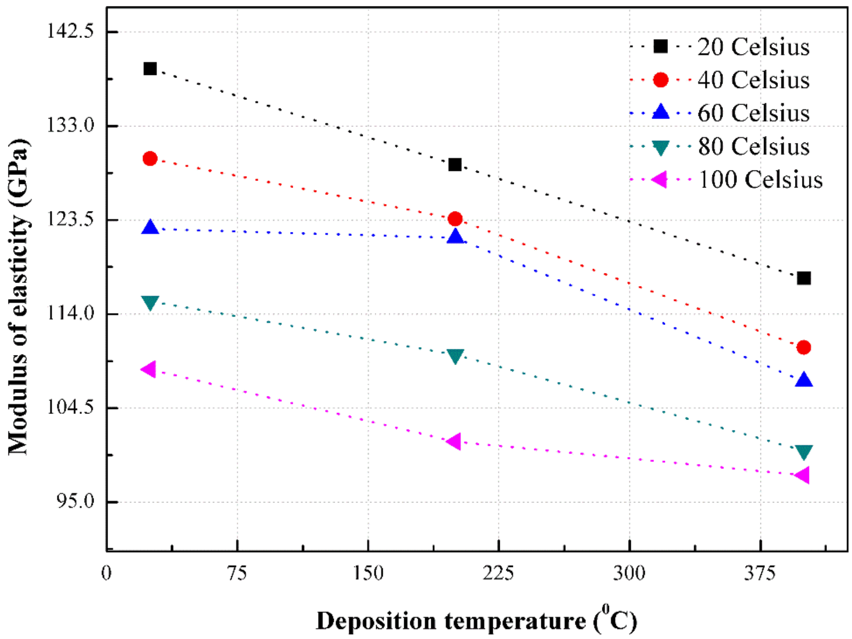


Figure 3. The fluctuation of the modulus of elasticity for niobium nitride thin films deposited at different substrate temperatures and tested at temperature between 20 and 100 ºC.

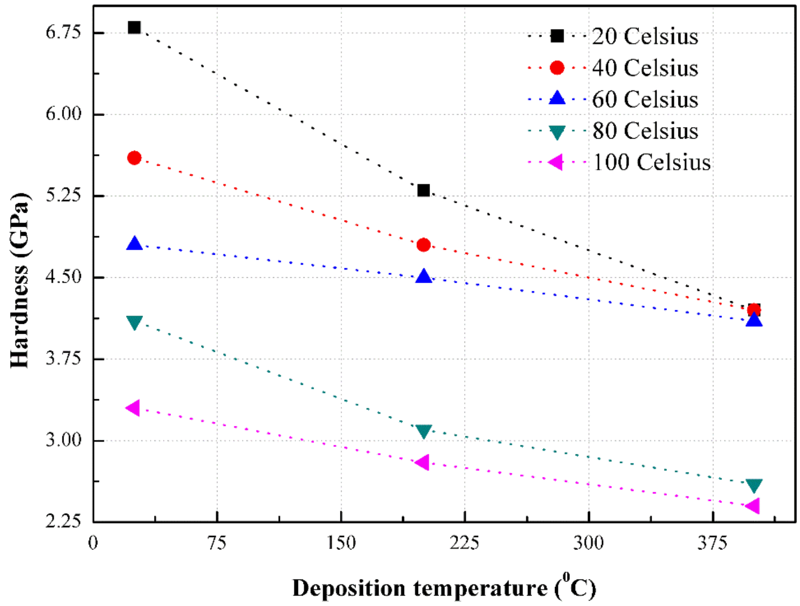


Figure 4. Hardness for niobium nitride thin films tested at temperatures between 20 and 100 ºC.

The hardness of the thin films is another mechanical property of interest. The hardness fluctuation for the deposited niobium nitride thin films investigated at temperatures between 20 and 100 ºC is graphically given in Figure 4. In general, the same trend as for the modulus of elasticity can be observed. We must bring out into relief that the decrease of hardness with the increase in testing temperature up to 100 ºC is much more pronounced. This decrease is about 51 % in the case of the films deposited at room temperature and 43 % in the case of the films deposited on substrates preheated at 400 ºC. When discussing about the same testing temperature, the hardness is still decreasing but the decrease is less accentuated, varying between 15 % (for testing temperature of 60 ºC) and 38 % (for testing temperature of 20 ºC). When tested at 20 ºC, the hardness ranged between 4.2 GPa for the films deposited at 400 ºC and 6.8 GPa for the films deposited at room temperature.

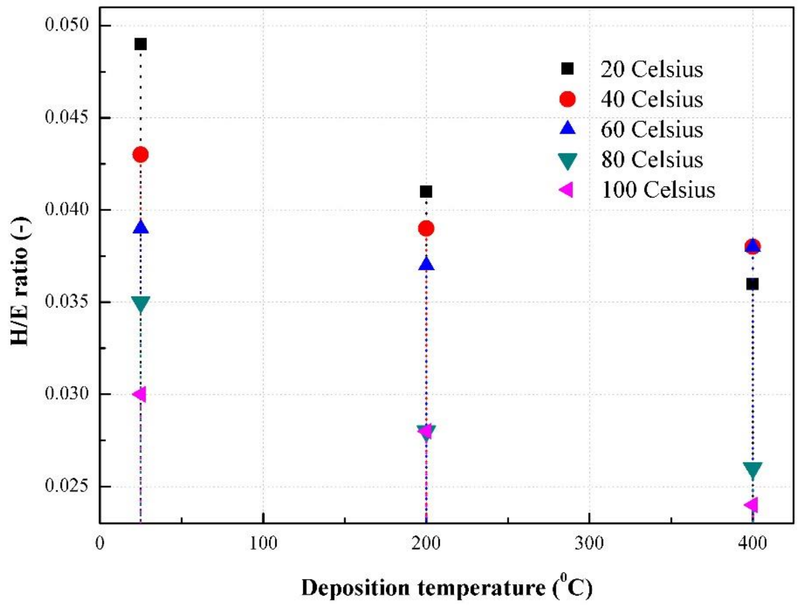


Figure 5. Fluctuation of the hardness/modulus of elasticity ratio for the investigated niobium nitride thin films tested at temperatures between 20 and 100 ºC.

The hardness/modulus of elasticity ratio was calculated for each sample to determine the material characterized by the best mechanical behaviour. The fluctuation of this ratio is given in Figure 5. We notice that the value of this ratio decreases, in general, with the increase in testing temperature from 20 ºC to 100 ºC regardless of the deposition temperature. Its values ranged between 0.024 and 0.049. The niobium nitride thin films deposited on silicon substrate at room temperature and tested at 20 ºC present the highest value of the ratio and, implicitly, are characterized by the best mechanical characteristics.

The change in niobium nitride thin films properties is probably due to their crystal structure that may contain different phases such as cubic δ-NbN, hexagonal β-Nb_2N, tetragonal γ-Nb_4N_3 and so on [7, 12, 13]. Moreover, the preheating of the substrate at 200 and 400 ºC induces some thermal stresses which also affect the structure of the deposited materials.

4. Conclusions

Niobium nitride thin films were deposited by DC magnetron sputtering on silicon substrates at temperature between 25 and 400 ºC. The films were further investigated by atomic force microscopy analyses. We determined that the increase in deposition temperature led to the obtaining of rough surfaces. The highest mechanical characteristics are specific to the niobium nitride thin films deposited at room temperature. The modulus of elasticity and the hardness decreased with the increase in both deposition temperature and testing temperature. However, the testing temperature had a stronger downward effect than the deposition temperature, leading to a decrease of up to 50 % of the hardness. We assume that the crystal structure of the deposited films and the thermal stresses are causing the change in these properties.

5. References

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