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Temperature effect on the mechanical characteristics of niobium nitride thin films

V Merie1, M Pustan2, G Negrea1, C Bîrleanu2 and F Șerdean2
1 Department of Materials Science and Engineering, Technical University of Cluj-Napoca, Cluj-Napoca, 400641, Romania
2 Department of Mechanical Systems Engineering, Technical University of Cluj-Napoca, Cluj-Napoca, 400641, Romania
E-mail: violeta.merie@stm.utcluj.ro

Abstract. The mechanical, physical, chemical and tribological properties of niobium nitride thin films are making them suitable for a wide range of applications such as protective coatings, microelectronics and so on. The paper has two main goals: (a) the deposition of niobium nitride thin films by direct current magnetron sputtering on silicon Si (100) substrates and (b) the highlighting of temperature influence on their mechanical properties. The films were deposited at different nitrogen flow rates ranged between 0 and 2.2 cm³·min⁻¹. The deposition time and temperature, argon flow rate, discharge current, pressure and the distance between the substrate and the target were kept constant. The so-obtained coatings were further investigated by atomic force microscopy analyses to determine their topographical and mechanical properties namely the hardness and the modulus of elasticity. The tests were performed at temperatures between 20 °C and 100 °C while the relative humidity was kept constant. The results pointed out that both the modulus of elasticity and the nanohardness of the films decreased with the increase in testing temperature. The increase in nitrogen flow rate up to 1.65 cm³·min⁻¹ went hand in hand with the increase in both mechanical properties.

1. Introduction
The use of niobium nitride in a wide range of application is attributed to its mechanical, physical, chemical, electrical and tribological properties [1]. This material shows high hardness, good superconducting and tribological properties, excellent corrosion resistance, high melting point, thermal stability and so on [2, 3]. It can be used as tunnel junctions, hard and protective coatings, in microelectromechanical systems (MEMS), microelectronics etc. [4-6].

Niobium nitride thin films can be obtained by different techniques. Magnetron sputtering is often used for depositing such coatings [7, 8]. Besides this technology, the literature reports that niobium nitride films were also obtained by pulsed laser deposition, high temperature chemical vapor deposition, thermal diffusion method, cathodic arc deposition and other methods [4, 9]. The properties of the deposited films are strongly influenced by a number of factors such as the substrate material, nitrogen flow rate, pressure, deposition time and so on.

The present research is a study regarding the niobium nitride thin films deposited by direct current (DC) magnetron sputtering at different nitrogen flow rates. The paper aims at highlighting the influence of the testing temperature of the mechanical characteristics of the investigated niobium nitride films.
2. Materials and experimental procedure

The niobium nitride thin films were deposited by DC magnetron sputtering on silicon Si (100) substrates. A niobium target with a purity of 99.95% was employed. First, the silicon substrates were cleaned in an ultrasonic bath with acetone and isopropyl alcohol and blown with compressed air to remove any possible impurities.

The deposition was done in a reactive sputtering facility from the Materials Science and Engineering, Technical University of Cluj-Napoca, with a base pressure of 10^-7 torr. The atmosphere inside the chamber was a mixture of argon and nitrogen. The argon flow rate was 40 cm³·min⁻¹. The discharge current and the pressure were kept constant at 350 mA and 2 mtorr respectively. A distance of 60 mm was maintained between the niobium target and the silicon substrates. All the samples were deposited for 20 minutes at room temperature (the substrates were not preheated). The nitrogen flow rate was ranged between 0 and 2.20 cm³·min⁻¹. The thickness of the deposited films was determined using a JEOL 5600LV microscope. Its determined value was about 0.35 µm.

The deposited niobium nitride thin films were characterized using a XE 70 atomic force microscope (AFM) from the Micro and Nano Systems Laboratory, Technical University of Cluj-Napoca. The topography of each sample was studied by scanning them in the non-contact mode of the microscope using a PPP-NCHR cantilever. The nanoindentation tests were performed using a TD23838 nanoindentor. The nanoindentor was charged at a force limit of 50 µN and the set point was 5 µN. The mechanical properties of the deposited niobium nitride thin films were determined at different temperatures namely 20, 40, 60, 80 and 100 ºC respectively. The tests were performed at a relative humidity of 20 %.

3. Results and discussions

Once the niobium nitride thin films were deposited, they were further investigated by atomic force microscopy analyses. We used the scanning in the non-contact mode and the nanoindentation mode of the atomic force microscope.

First, the topography was studied. After scanning all the samples in non-contact mode, 3D images and the roughness parameters of each film were obtained using the XEI Image Processing Tools for SPM data. The values of the average roughness, \( R_a \), and the average maximum height of the profile, \( R_z \), determined at a testing temperature of 20 ºC are presented in table 1. The smallest nitrogen flow rate (0.55 cm³·min⁻¹) determines a strong decrease of the average roughness from 0.941 to 0.133 nm. Further, the increase in nitrogen flow rate up to 2.20 cm³·min⁻¹ is accompanied by the increase in this roughness parameter up to 1.202 nm. The increase is more significant when the nitrogen flow rate was increased from 1.65 to 2.20 cm³·min⁻¹.

| Nitrogen flow rate (cm³·min⁻¹) | \( R_a \) (nm) | \( R_z \) (nm) |
|------------------------------|----------------|----------------|
| 0                           | 0.941          | 10.584         |
| 0.55                        | 0.133          | 1.583          |
| 1.10                        | 0.544          | 10.953         |
| 1.65                        | 0.633          | 8.546          |
| 2.20                        | 1.202          | 11.686         |

Nanoindentation tests were performed to determine the nanohardness and the modulus of elasticity of each sample. After these tests, we obtained force vs. Z scan curves like that presented in figure 1. These curves were interpreted using two models. First, the Oliver and Pharr method was employed to determine the nanohardness of the films. This method assumes that the nanoindentation tests determine both elastic and plastic deformations in the tested materials. Secondly, the Hertzian model allowed us to determine the modulus of elasticity. Compared to the Oliver and Pharr model, the Hertzian model assumes that the nanoindentation leads only to elastic deformation.
Figure 1. A force vs. Z scan curve obtained after a nanoindentation test on a niobium nitride thin film deposited at a nitrogen flow rate of 1.65 cm$^3$·min$^{-1}$.

Figure 2 shows the fluctuation of the nanohardness in terms of nitrogen flow rate and testing temperature. When we discuss about the same testing temperature, this mechanical characteristic increased with the increase in nitrogen flow rate up to 1.65 cm$^3$·min$^{-1}$ after which it decreased. This trend decreased in intensity as the temperature has risen. Instead, if we consider that the nitrogen flow rate is kept constant, the increase in testing temperature up to 100 ºC lead to a strong decrease of the nanohardness. The highest decrease was marked out for the niobium nitride thin films deposited at 1.65 cm$^3$·min$^{-1}$ when it ranged between 0.94 GPa (at 100 ºC) and 3.90 GPa (at 20 ºC). In general, the decreased in nanohardness was higher than 64 %. When the nanoindentation tests were performed at a temperature of 100 ºC, the nanohardness of the investigated niobium nitride thin films didn’t exceed the value of a 1 GPa.

Figure 2. Nanohardness of the niobium nitride thin films deposited at different nitrogen flow rates.

A similar trend as marked out for the nanohardness was also obtained for the modulus of elasticity. We assume that the change in the mechanical properties is due to the structure and composition of the
films. Practically, their structure contains hexagonal and cubic constituents [10]. Thus, the mechanical properties may vary depending on the quantities of these constituents.

The nanohardness/modulus of elasticity ratio was computed to establish the niobium nitride thin films characterized by the best mechanical behaviour. The values determined for all five types of films tested at temperatures from 20 to 100 °C are given in table 2. A decreasing trend can be observed with the increase in testing temperature regardless of the nitrogen flow rate. When the testing temperature is kept constant, the increase in nitrogen flow rate is accompanied by the increase in this parameter up to a nitrogen flow rate of 1.65 cm³·min⁻¹. This phenomenon is more significant at 20 °C when the ratio almost doubles its value (from 0.043 to 0.080). A further increase in nitrogen flow rate leads to a decrease of the nanohardness/modulus of elasticity ratio. The niobium nitride thin films deposited at a nitrogen flow rate of 1.65 cm³·min⁻¹ present the highest values of the ratio at each testing temperature, with bringing up that the maximum value is specific to a testing temperature of 20 °C.

| Nitrogen flow rate (cm³·min⁻¹) | Nanohardness/Modulus of elasticity ratio, H/E (−) |
|--------------------------------|-----------------------------------------------|
| 20 °C                          | 40 °C                          | 60 °C                          | 80 °C                          | 100 °C                          |
| 0                              | 0.043                          | 0.031                          | 0.028                          | 0.026                          | 0.018                          |
| 0.55                           | 0.055                          | 0.041                          | 0.031                          | 0.026                          | 0.021                          |
| 1.10                           | 0.066                          | 0.049                          | 0.035                          | 0.031                          | 0.025                          |
| 1.65                           | 0.080                          | 0.058                          | 0.040                          | 0.031                          | 0.025                          |
| 2.20                           | 0.062                          | 0.048                          | 0.033                          | 0.028                          | 0.022                          |

4. Conclusions
Niobium nitride thin films were deposited by DC magnetron sputtering on silicon substrates at nitrogen flow rates between 0 and 2.20 cm³·min⁻¹. The so-obtained films were characterized by atomic force microscopy investigations at different testing temperatures. The average roughness has increased almost ten times with the increase in nitrogen flow rate up to 2.2 cm³·min⁻¹. The mechanical characteristics have increased up to a nitrogen flow rate up to 1.65 cm³·min⁻¹ after which they decreased. A continuous decrease in nanohardness and modulus of elasticity has been noticed when the testing temperature has been increased from 20 to 100 °C. The best mechanical behaviour was marked out on the films deposited at 1.65 cm³·min⁻¹, mainly the films tested at room temperature.

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