The influence of deposition time and testing temperature on mechanical properties of niobium nitride thin films

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Abstract. This paper is focused on studying the effects of testing temperature on the mechanical properties (hardness and modulus of elasticity) of niobium nitride thin (NbN) films. In this respect, NbN thin films were deposited on silicon substrate at room temperature by direct current magnetron sputtering using a niobium target of high purity. All the films were deposited on non-biased substrates. The deposition time was ranged between 10 and 40 minutes. Thus, we’ve obtained four types of samples deposited at different deposition times namely 10, 20, 30 and 40 minutes. The mechanical properties of these thin films such as the modulus of elasticity and hardness were investigated using the nanoindentation mode of the atomic force microscopy. The experimental tests were carried out by varying the testing temperature. The purpose of this analysis was to determine the change in mechanical characteristics of NbN films when the testing temperature was varied from room temperature up to 100 °C. The outcome of this investigation points out that the change in testing temperature has a significant influence on the mechanical properties of NbN thin films. The results also allowed us to determine the films characterized by the best mechanical behaviour.

1. Introduction
The niobium nitride (NbN) thin films have excellent mechanical properties, superconducting transition temperature, high melting point and electrical conductivity. They are used in different applications such as communication devices, absorbing of antireflective coatings, photo-catalysts and so on due to the characteristics mentioned before.

In the latest research, NbN has become very popular mostly due to its high hardness, wear resistance and chemical inertness but more important the thermal stability, which makes it a perfect choice for different applications in fields such as micromechanics or optics [1, 2]. The NbN thin films can be used as protective coating, diffusion barrier or field emission cathode for most microelectronic devices [3]. Also, the superconducting properties of NbN have been highlighted in low temperature superconducting electronics such as tunnel junctions [4] or nano-structured X-ray detectors [5, 6].

Various deposition techniques for obtaining the NbN thin films which include reactive magnetron sputtering, ion beam assisted deposition, pulsed laser deposition, cathodic arc deposition, high temperature chemical vapor deposition [7], thermal diffusion [8, 9], cathodic arc physical vapor deposition [10], thermal processing [11], atomic layer deposition and many more are reported. The mechanical properties of the deposited NbN are strongly determined by a set of parameters and factors, such as the deposition time and temperature, the pressure, the nitrogen and argon flow rates,
the discharge current and so on. This paper’s main aim is to investigate the deposition time and testing temperature influence on the mechanical properties of four samples consisting in thin solid films of NbN, research that has not been reported in the open literature.

2. Materials and experimental procedure

2.1. Materials and experimental deposition

The deposition of the thin films was conducted by DC magnetron sputtering and one layer of NbN was deposited on a silicon Si (100) substrate of 10 mm x 10 mm using a Nb target with a purity of 99.95%. The deposition process was carried on in a mixture of Ar and N in a high vacuum chamber (10⁻⁷ torr). The following deposition parameters were kept constant: discharge current (Iₐ), argon flow rate (Qₐ), nitrogen flow rate (Qₙ₂) and pressure (P). Moreover, all samples were deposited at the same temperature, T. Using a JEOL 5600LV electron microscope the thickness of the obtained thin films was determined, and it varied between 0.18 µm and 0.70 µm. The values of the deposition parameters are presented in table 1 and, as it can be seen, the deposition time varied between 10 and 40 minutes.

| Sample    | T (°C) | Time (min) | P (mtorr) | Iₐ (mA) | Qₐ (cm³/min) | Qₙ₂ (cm³/min) |
|-----------|--------|------------|-----------|---------|--------------|---------------|
| NbN_10    |        | 10         |           |         |              |               |
| NbN_20    | 20     | 20         |           |         |              |               |
| NbN_30    | 30     | 2.1-2.2    | 300       | 40      | 1.5          |               |
| NbN_40    |        | 40         |           |         |              |               |

2.2. Nanoindentation

The mechanical characterization of the deposited thin films was carried out by atomic force microscopy investigations. The experimental tests were conducted using the XE 70 Atomic Force Microscope (AFM) from the Micro and Nano Systems Laboratory from the Technical University of Cluj-Napoca.

The relative humidity was kept constant (28 %) while the testing temperature was varied between 20 °C and 100 °C. Each sample was heated using a Peltier device until its temperature stabilized at the desired testing value (20 °C, 40 °C, 60 °C, 80 °C and 100 °C, respectively). The tests were performed using a TD 23838 nanoindentor which, according to the manufacturer specifications has a frequency of 50 kHz, a stiffness of 272 N·m⁻¹, a thickness of 41 µm, a length of 1050 µm, a height less than 90 µm and a tip radius smaller than 25 nm. The tests were performed for a force limit of 50 µN.

First, each sample surface was scanned at 28 %RH and at ambient temperature with the AFM cantilever in contact mode in order to obtain the topography of the samples. Then, the samples were characterized from the mechanical point of view by performing nanoindentation. The technique consists in pressing the hard Berkovich tip into the sample until it penetrates the sample and the maximum load is reached. Based on the performed nanoindentation tests, the Z scan vs. force curves characteristic to each deposited sample were obtained. In order to obtain the nanohardness the Oliver and Pharr method was employed.

This method is based on the assumption that only plastic deformation occurs during the experimental tests. In opposition, the Hertzian method is based on the assumption that only elastic deformation occurs during nanoindentation allowing to determine Young’s modulus.
3. Results and discussions
First, the topography of the samples was obtained. Figure 1 presents a 3D image of the NbN thin film deposited for 20 minutes. The purpose of this scanning was to allow performing the nanoindentation in points without defects.

![Figure 1. 3D image of the NbN_20 sample.](image)

![Figure 2. Image of the XEI Image Processing Tools for SPM Data for determining the nanohardness of the NbN_20 sample.](image)
3.1. Nanohardness

The characterization of each sample from the mechanical point of view consisted in determining the nanohardness and the modulus of elasticity for each thin solid film. Figure 2 presents an image of a Z scan vs. force curve given by the XEI software. The image is for the nanoindentation performed in the third point of the sample of NbN deposited for 20 minutes.

![Figure 2](image2.png)

**Figure 2.** Nanoindentation curve for NbN thin films.

The experimental tests were conducted in several points of each sample and the average values were computed. The variation of the nanohardness with respect to the deposition time is illustrated in figure 3 for the samples tested at 20 °C. It can be seen that the deposition time influences the nanohardness of the thin films. The nanohardness increases with 32% when the deposition time increases to 30 minutes. The dramatic decrease of the nanohardness of the sample deposited for 40 minutes was caused by the Nb$_2$N that formed during the deposition of this sample and that was identified using X-Ray Diffraction analyses.

![Figure 3](image3.png)

**Figure 3.** Nanohardness vs. deposition time for NbN thin films.

The experimental investigations were also conducted in multiple points for each sample when the testing temperature varied between 20 °C and 100 °C. The average values of the nanohardness showed a decreasing trend for all deposited thin films except for the one deposited for 40 minutes (see figure 4) due to the occurrence of Nb$_2$N. A mild decrease of about 18 % and 21 % in the average values of the nanohardness can be observed for the samples deposited for 10 and 30 minutes, respectively, while a considerable decrease of about 48 % can be observed for the average nanohardness of the sample deposited for 20 minutes.

![Figure 4](image4.png)

**Figure 4.** Nanohardness vs. testing temperature for all deposited thin films.
3.2. Young’s modulus
The second mechanical characteristic that presented interest for this study is Young’s modulus. It was determined using the Hertzian method for interpreting the Z scan vs. force curves provided by the XEI software. The experimental tests were again conducted in several points of each sample and the average values were computed. The variation of the modulus of elasticity with respect to the deposition time is presented in figure 5 for all the samples tested at 20 °C. A similar increasing trend can be observed as in the case of the nanohardness with the same exception, namely, the sample deposited for 40 minutes, which has the lowest modulus of elasticity.

![Figure 5. The variation of Young’s modulus determined at 20 °C with respect to deposition time.](image)

| Sample  | Temperature (°C) | 20  | 40  | 60  | 80  | 100 |
|---------|------------------|-----|-----|-----|-----|-----|
| NbN_10  |                  | 47.81 | 46.61 | 46.58 | 46.18 | 45.78 |
| NbN_20  |                  | 51.19 | 50.38 | 48.03 | 47.52 | 46.10 |
| NbN_30  |                  | 51.99 | 50.09 | 49.64 | 47.5  | 46.76 |
| NbN_40  |                  | 47.33 | 46.95 | 46.52 | 47.74 | 49.90 |

The average values of this mechanical characteristic from several test points for each testing temperature were also determined and the results are presented in table 2. As it can be seen the values decrease for the samples deposited for 10, 20 and 30 minutes, respectively, but with smaller percentages when compared to the nanohardness. Again, the values for the NbN_40 sample do not respect this decreasing trend probably due to the same reason (the existence of Nb_2N).

3.3. Nanoharness/Young’s modulus ratio

| Sample  | NbN_10 | NbN_20 | NbN_30 | NbN_40 |
|---------|--------|--------|--------|--------|
| H/E     | 0.066  | 0.066  | 0.080  | 0.048  |

This ratio has to be computed in order to determine the thin film characterized by the best mechanical behavior. The values of this ratio (H/E) computed for the characteristic values obtained at 20 °C are
given in table 3. It has to be noted that the first two samples have that the value of the H/E ratio. The highest value of this ratio (0.080) is obtained for the film deposited for 30 minutes. We assume that the increase in time deposition up to 30 minutes determines an increase of the thin film thickness and better values for the mechanical properties.

4. Conclusions
The deposition of several samples of NbN thin films was conducted by magnetron sputtering on silicon substrates for different periods of time (10, 20, 30 and 40 minutes). The experimental investigations performed using the AFM showed an increase of the nanohardness and the modulus of elasticity when the deposition time increased up to 30 minutes. The NbN_40 sample did not respect the trend due to the forming of Nb_2N during deposition.

Also, the influence of testing temperature on the mechanical properties was studied. The increase of the testing temperature from 20 to 100 °C determined a decrease of both nanohardness and modulus of elasticity values for all studied samples except NbN_40 due to the already mentioned reason. The obtained results showed that the thin films deposited for 30 minutes are characterized by the best mechanical behaviour.

5. References
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