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# Investigation of the Structural, Electrical and Corrosion Properties of NbN Films Deposited by Magnetron Sputtering (DC Power Supply) Technique at Different Power

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This study aims to deposit niobium nitride (NbN) thin films on stainless steel (SS304) and silicon (100) substrates using direct current (DC) magnetron sputtering method at different power (varied from 100 to 150 W). The film structure is analyzed by X-ray diffraction (XRD); the patterns show that the films possess a (111) preferred orientation, corresponding to the cubic structure phase. Rutherford elastic backscattering (RBS) and energy dispersive X-ray (EDX) are used to investigate the composition of the prepared films. Surface morphology of the films is explored by scanning electron microscopy (SEM) and atomic force microscopy (AFM) images. AFM images clarify modifications of the morphology, especially roughness versus increased power, where roughness decreased with increasing thickness as well as power. Corrosion and microhardness performances of the films are related and assigned to the crystallinity of samples, which varies with power. Corrosion resistance of NbN films associated with SS304 substrates is improved. These attractive results may allow to use our films in the field of medical tools or equipment (equivalent to saline serum media). Electrical measurements (*C-V* and *I-V*) of films deposited at a power of 100 W confirm the potential electrical applications of NbN films deposited by DC sputtering method.

**Keywords:** NbN film, Power effect, Structural, Corrosion, Electrical Characterization.

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## 1. INTRODUCTION

Metal nitride films like NbN [1], ZrN [2], TiN [3] and CrN [4] possess high hardness, interesting tribological behavior, good wear, corrosion resistance and good thermal stability. In addition, they can be used in corrosive and high temperature environments. Zirconium nitride thin films were deposited using vacuum arc discharge at different $N_2$ partial pressure ratios by Abdallah et al. [2]. They studied the effect on microhardness, grain size, crystallographic quality, stress and stoichiometry developed in the films. TiN thin films were synthesized on different substrates by means of vacuum arc discharge method [5]. The prepared TiN films have N/Ti ratio of around 1, with low levels of contamination elements. Also, titanium nitrides TiN and TiAlVN were deposited by sputtering [3], and these alloys were found to be an effective method to enhance the corrosion resistance of stainless steel 304 [6].

Specifically, NbN thin films are used in a variety of applications such as cutting tools, high melting points and protective coatings in the food and medical industries, automotive industry and microelectronics like superconductor films [7], construction of all refractory Josephson tunnel junctions and integrated circuits for device applications [8]. Also, they operate below the NbN superconducting critical temperature $T_c$, which varies from 40 to 5 K depending on the film (thickness and quality), as well as on the appropriate substrate (single crystal and epitaxial growth) [9]. Chockalingam et al. [10] measured the superconductor properties of epitaxial NbN films developed on a single crystal MgO substrate (100) oriented under different conditions using reactive magnetron sputtering (power effect and nitrogen ratio), and they found that $T_c$ increases with increasing power. Xin-kang et al. [7] investigated the structural properties of deposited NbN films as a function of temperature, they obtained the cubic phase. This behavior agrees with the result of Kavitha et al. [8], who studied the effect of power on the thickness and structural properties of NbN films, where the thickness increases with increasing power (from 60 to 120 W) due to an increase in the ionic energy of sputtered particles. Sandu et al. [9] studied in detail the hardness and its relation to the crystallographic phase, as well as the grain size. Zenghu et al. [10] observed a decrease in microhardness with an increase in nitrogen percentage.

Physical vapor deposition (PVD) processes have interesting wide industrial applications. Magnetron sputtering [8] is frequently used due to its advantages, plasma parameter adjustment [6] and the ability to control thickness [11] with high quality [10], large surface area homogeneity, hardness and corrosion behavior of deposited films [12], but another deposition technique requires heating up to 500 °C, such as plasma enhanced chemical vapor deposition (PECVD) [13]. Furthermore, corrosion behavior of thin films is an interesting property for use in industrial and medical fields [14]. Local impact in the form of pits, crevices, intergranular corrosion or cracks can occur largely due to an increase in the film surface roughness. This high resistance has led to the use of a nitride film as a protective layer, as well as an anti-corrosion and wear-resistant coating in industry and areas such as airspace, automotive, marine transport [3].

The aim of present study is to investigate the mechanical behavior (microhardnesss and corrosion) and crystalline properties of NbN films obtained by magnetron sputtering technique at different power on Si (100) and S304 substrates, since this technique shows great versatility in both the deposition rate and the film thickness, when the source power can be adjusted. SEM and EDX analysis

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were applied to explore the morphology and content of elements in films. There is the possibility of utilizing the prepared films as a protective layer against aggressive media. Electrical studies were performed for a thinner NbN film deposited on Si (100) at 100 W.

## 2. EXPERIMENTAL CONDITIONS

DC power supply magnetron sputtering was used to deposit NbN films at a power of 175, 200 and 225 W. High-purity target Nb (99.99 %) was used at a diameter of 5 cm in plasma gas $N_2$/Ar mixture (60/40) and the substrate temperature was 1000 °C. The target/substrate distance and pressure were kept at 5 cm and 4 mTorr, respectively. A vacuum chamber (cylindrical, made of stainless steel 316, fabricated on site) was evacuated by a turbomolecular pump down to the residual pressure below $2 \cdot 10^{-6}$ Torr. The films were deposited on two types of substrates: Si (100) and SS304. The film quality is related to the parameters of the deposition process that can be optimized to obtain stoichiometric NbN films. Film thickness and morphology were measured ex situ by means of SEM (TESCAN Vega, XMU, Czech Republic). EDX was used to determine the chemical composition of the synthesized structures. The crystallinity of the films was analyzed by a Stoe Transmission X-ray diffractometer Stadi P using XRD ($\theta$-$2\theta$ scan mode with CuK$\alpha$ radiation).

The microhardness measurements were performed with a Vickers indenter (using an HX-1000 microhardness tester) [3] with a loading of 10 g for NbN/SS304 samples. Corrosion of NbN coatings deposited on SS304 substrate (NbN/SS304) was studied using the corrosion potential (Cor. Pot) by the Tafel method [14], polarization resistance, and electrochemical impedance spectroscopy (EIS) techniques [15] by means of Voltalab PGZ 301 (France), where the saline medium was 0.9 % NaCl (equivalent to serum media).

Measurements of the resistivity $R$ dependence of a thinner NbN film (deposited at 100 W) on temperature $T$ were performed using the standard, four-probe technique in a liquid nitrogen cryostat. A superconducting transition was observed in the studied film (deposited at 100 W). A QuadTech low voltage chip component test fixture attached to the Al electrodes on top and to the $p$-Si, constituting the bottom electrode, made connections to the sample. The electric transport was studied by obtaining the $C$-$V$ and $I$-$V$ characteristics using an HP 4192A Impedance Analyzer, QuadTech 1920 LCR Meter and Keithley 237 Source Measure unit [16].

## 3. RESULTS AND DISCUSSION

### 3.1 SEM Analysis

The films deposited on Si (100) were characterized by cross-sectional SEM to obtain information about thickness. It was found that the films have a dense structure, with a thickness of about 275 nm (Fig. 1a, b) at 100 W for secondary electrons and electron backscattering. The thickness increases with increasing DC power, this behavior was consistent with the results of Kavitha et al. [8], who found that the thickness of NbN film increases from 200 to 500 nm with increasing power

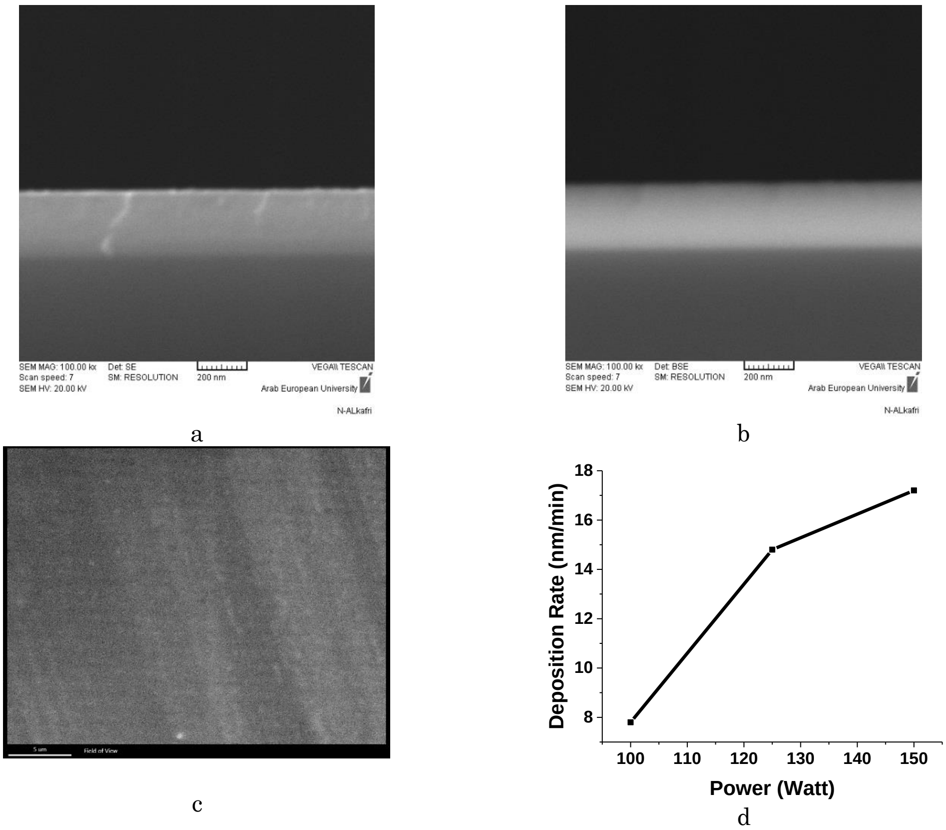



**Fig. 1** – SEM cross section of NbN film/Si at 100 W for secondary electrons and electron backscattering (a, b), SEM top view of the film deposited at 150 W (c), and deposition rate as function of power (d)

from 60 to 120 W. Fig. 1c shows a SEM view of the surface of NbN/Si film deposited at 150 W at 10k magnification, where the average grain size is about 75 nm.

The corresponding deposition rate (thickness/time) was varied in the range from 8 to 17 nm/min (Fig. 1d). An increase in the deposition rate with increasing power is due to an increase in the ion bombardment energy [17] for NbN film, as well as for ZnO film [17] using magnetron sputtering.

### 3.2 EDX and RBS Analysis

Table 1 and Fig. 2 show EDX results of the films for different power, which confirm the stoichiometry of NbN film, where Nb and N are the main components. However, there is little oxygen contamination (less than 10 %) due to residual air adsorbed in the deposition chamber. Also, the temperature of the deposited films was 100 °C (not in height), as we found in the previous work [18], with an increase in temperature for TiN film, a decrease in oxygen contamination in the chamber, as well as in the deposited film. In addition, the NbN film structure using XRD grows according to the chemical formula (next paragraph).

**Table 1** – EDX components of NbN films deposited at different power (100, 125 and 150 W)

| Element | 100 W | 125 W | 150 W |
|---|---|---|---|
| | Atomic % | Atomic % | Atomic % |
| N K | 58.31 | 62.07 | 50.13 |
| O K | 8.5 | 9.87 | 10.69 |

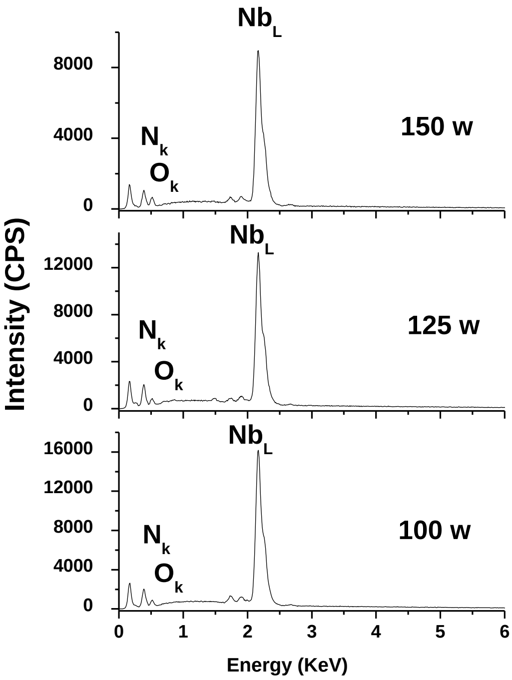
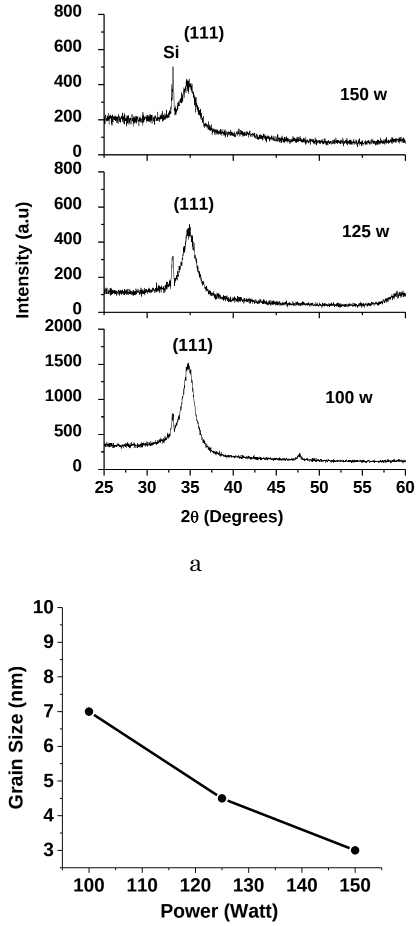



**Fig. 2** – EDX spectrum of NbN/Si film at different power

### 3.3 Structural Characterization (XRD)

The spectra of the films deposited show a diffraction peak at 34.70° that is assigned to (111) crystallographic preferred orientation in NbN/Si film (Fig. 3a), corresponding to the cubic phase according to JCPDS card number 89-5007. The grain size of the films was calculated using the Scherrer formula [12] for the preferred orientation. Whereas the grain size of (111) and peaks of CrN films deposited on Si (100) decrease from 7 to 3 nm with increasing power from 100 to 150 W. Xinkang et al. [7] obtained the same cubic phase, when they deposited NbN film at different temperatures.




b

**Fig. 3** – XRD pattern for CrN/Si films (a), grain size for deposited films a function of the power (b)

### 3.4 Corrosion Study: Potential Dynamic Polarization (Tafel)

The studies were carried out in sea water solution (0.9 % NaCl) at a temperature of 37 °C; chlorine ions provoked corrosion in saline medium, the scan rate was 1 mV/s and the electrode potential was increases from – 1000 to + 300 mV. The critical parameters like $E_{corr}$ and $I_{corr}$ were evaluated from the Tafel plots [3]. The corrosion behavior of NbN/SS304 films was compared to the uncoated reference SS304 sample. Fig. 4 shows the polarization curve and its Tafel fit for the uncoated sample (SS304 substrate) and NbN/SS304 films deposited at different power. The electrochemical parameters in the Tafel method are characterized and listed in Table 2, the current density $I_{corr}$ of coated films was lower than that of the uncoated sample (SS304) equal to 174 μA/cm$^2$. The value of $I_{corr}$ decreases from 17.45 to 6.313 μA/cm$^2$ with increasing power from 100 to 150 W, where a lower current density corresponds to a higher corrosion resistance. We can associate a higher corrosion resistance (of NbN/SS304 at 150 W) with a smaller grain size [6], as well as a higher microhardness [14], so the best corrosion resistance was for a film deposited at 150 W in the Tafel measurement.

The efficiency of NbN film deposited on the SS304 substrate at 150 W is determined by the formula:

$$Pi\% = \left(1 - \frac{i_{corr}}{i_{0corr}}\right) * 100 = \left(1 - \frac{6.313}{174}\right) * 100 = 96.37\ \%,$$

where $I_{corr}$ is the current density of the film and $I_{0corr}$ is the current density of the SS304 substrate. It is about 96.37 % compared to the uncoated sample, indicating that the film is more resistant to the SS304 substrate.

Benmoussat et al. [20] found that the current density increases and the corrosion resistance decreases for low carbon steel with increasing temperature of the electrolyte solution that contacts the steel. Also, they found that $I_{corr}$ decreases from 26.686 to 3.137 μA/cm$^2$ with increasing PH from 6.7 to 8 at 25 °C.

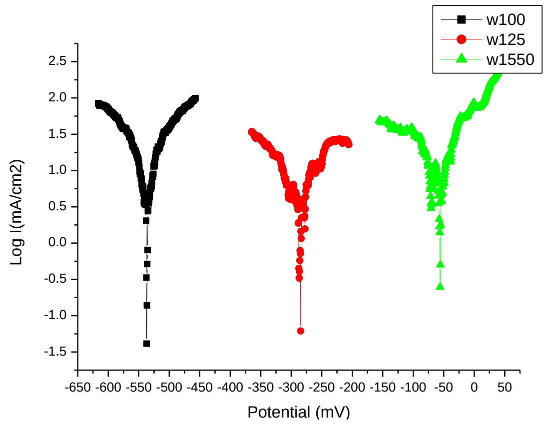



**Fig. 4** – Potential dynamic polarization curves (current/potential) of NbN/SS304 films at different power in 0.9 % NaCl

**Table 2** – Potential dynamic using Tafel fit for NbN/SS304 films deposited at different power in 0.9 % NaCl

| | $E$ ($i$ = 0), mV | $I_{corr}$, μA/cm$^2$ | $R_p$, kohm·cm$^2$ | Corrosion rate (mm/y) |
|---|---|---|---|---|
| 100 W | – 537.1 | 17.45 | 824.7 | 0.240 |
| 125 W | – 286.7 | 7.31 | 1.54 | 0.101 |
| 150 W | – 55.7 | 6.313 | 2.45 | 0.087 |

### 3.5 AFM Study

The variation of the RMS roughness (5×5 μm area) as a function of power for three NbN/Si films is presented in Fig. 5. A decrease in roughness with increasing power can occur due to an increase in energy and, consequently, sputtering of small atoms to make the film smoother.

### 3.6 Electrical Study

#### 3.6.1 *I-V* and *C-V* measurements

The *I-V* characteristics of Al/*n*-ZnS/Si films were obtained perpendicular to a thinner film (power 100 W), as shown in Fig. 6a. In general, the forward current is

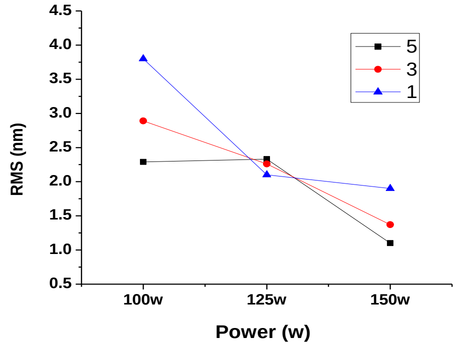
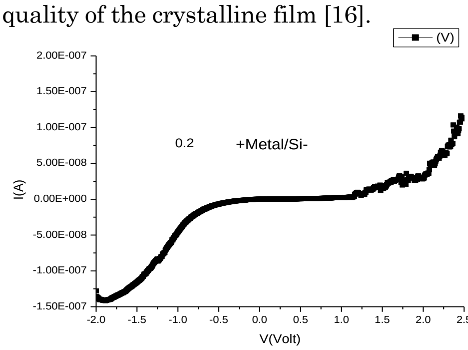



**Fig. 5** – The RMS roughness as a function of power for three NbN/Si films

generated due to the flow of majority carriers, whereby the applied bias voltage reduces the built-in potential and width of the depletion layer as the majority carriers are injected.

In the low voltage region between 0 and 2 V, a recombination current is generated when excitation electrons from the valence band to the conduction band recombine with holes existing in the valence band. Above 2 V, a tunneling current takes part, and then one can observe an exponential increase in the magnitude of the current (current diffusion) at higher forward voltages with a predominance of conductivity due to diffusion. With reverse bias, apart from the thickest 70-min film, the current generation process can be seen to occur at higher voltages (> 1.5 V) after the diffusion current takes over. It is notable that the improvement in the crystal quality (large grain size) is associated with a prominent and sharper *I-V* characteristic, as studied in our previous work [16].

For exploring the electrical behaviors of the grown NbN films, *C-V* characterization on the Al/NbN/Si MIS diodes was carried out using a Hewlett-Packard 4192A LF Impedance Analyzer by means of a small ac signal at a frequency varied from 10 kHz to 1 MHz with a forward bias applied to the Al gate electrode (positive) and Si (negative) as shown in Fig. 6b. The characteristics were recorded in a wide range of bias voltages between – 35 and 35 V and, as can be seen, with pronounced layers of accumulation, depletion and inversion. Capacitance has the highest value for a frequency of 10 KHz and decreases with increasing frequency up to 1 MHz. The accumulation capacitance decreases with increasing current from 0.0032 to 0.002 A and decreasing frequency from 10 kHz to 1 MHz. This decrease in the capacitance was also observed in previous work for AlN/Si and is related to the quality of the crystalline film [16].




a

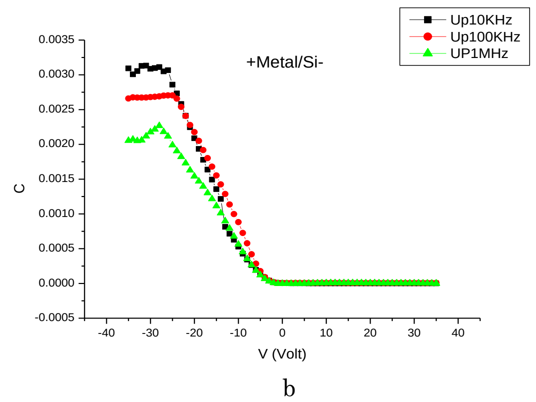



**Fig. 6** – *I-V* for a thinner film at 100 W (a), *C-V* measurement at different frequencies (10 kHz-1 MHz) (b)

### 3.5.2 Low Temperature Resistance Study

Fig. 7 shows the resistance *R* (in ohms) as a function of low temperature *T* (in kelvins) characteristics for NbN film deposited on Si (100) substrate at 100 W. It was found that $T_c$ (critical temperature) is about 37 K, we could explain this high value due to the studied film with a thickness of about 275 nm deposited on an unwanted substrate (MgO or $Al_2O_3$) or epitaxial growth ($T_c$ is less than 10 K in the presence of epitaxial film). Słysz et al. [9] investigated NbN films deposited on four types of substrates: single-crystal $Al_2O_3$, Si, $SiO_2$ and $Si_3N_4$. The $T_c$ values were obtained for ultrathin superconducting NbN layers (6 nm thick), and it was found that $T_c$ varied from 10 to 12 K, while for a 50 nm thick film it was about 14 K. Chockalingam et al. [10] showed the superconducting properties of epitaxial NbN/MgO film 50 nm thick under different power conditions using magnetron sputtering; they found that $T_c$ increased from 11 to 16 K with increasing power. This item is intended for direct presentation of the investigation results. The latter are presented in the form of mathematical expressions, plots, photographs, tables, etc. In this case, the usual statement of facts is not enough, and analysis is required. All numerical data should be presented in conventional units.

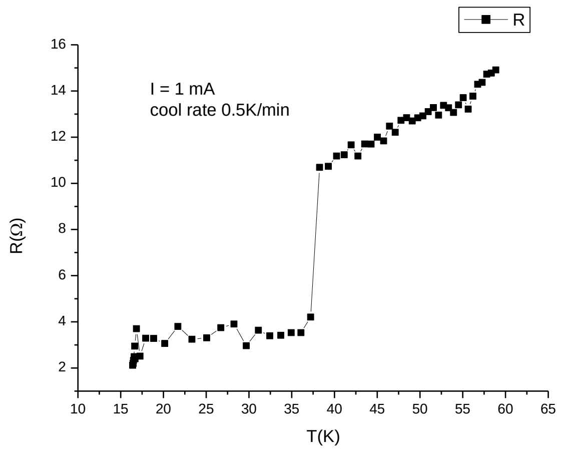



**Fig. 7** – Resistance *R* (in ohms) as a function of low temperature deposition on Si (100) substrate at 100 W

## 4. CONCLUSIONS

The microhardness behavior and crystalline properties of NbN films were investigated using the magnetron sputtering technique at different power on Si (100) and SS304 substrates. This method shows high versatility in both the deposition rate and the film thickness, when the source power can be adjusted. In order to study the morphology and content of elements in the obtained films, analysis by means of SEM and EDX was applied. It was also shown the possibility of using the prepared films as a protective layer against aggressive media on the basis of corrosion tests (potential dynamic and EIS). Corrosion measurements signified that the corrosion resistance of three NbN films deposited on SS304 substrates in physiological normal saline environment (0.9 % NaCl) was improved compared to SS304 substrates. These attractive results allow our films to be used in the manufacture of medical implants. *C-V*, *I-V* and resistivity measurements were performed for a thinner film deposited on the Si (100) substrate at 100 W. These measurements confirm the interesting properties of NbN films deposited by DC sputtering and prove potential electrical applications.

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## Дослідження структурних, електричних та корозійних властивостей плівок NbN, нанесених методом магнетронного напилення (живлення постійним струмом) при різних потужностях

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В статті вивчено нанесення тонких плівок нітриду ніобію (NbN) на підкладки з нержавіючої сталі (SS304) і кремнію (100) за допомогою методу магнетронного розпилення при постійному струмі та різних потужностях від 100 до 150 Вт. Структура плівки аналізується за допомогою рентгенівської дифракції (XRD); дифракційні картини показують, що плівки мають переважну орієнтацію (111), що відповідає фазі кубічної структури. Для дослідження складу підготовлених плівок використовуються метод пружного зворотного розсіювання Резерфорда (RBS) та енергодисперсійне рентгенівське випромінювання (EDX). Морфологія поверхні плівок досліджується за допомогою зображень, отриманих скануючою електронною мікроскопією (SEM) та атомно-силовою мікроскопією (AFM). Зображення AFM уточнюють зміни морфології, особливо шорсткість залежно від потужності; отримано, що шорсткість зменшується зі збільшенням товщини плівки, а також потужності. Показники корозії та мікротвердості плівок пов'язані та приписуються кристалічності зразків, яка змінюється залежно від потужності. Корозійна стійкість плівок NbN на підкладках з SS304 підвищується. Ці привабливі результати можуть дозволити використання отриманих плівок в області медичних інструментів або обладнання (еквівалент сольової сироватки). Електричні вимірювання (*C-V* та *I-V*) плівок, нанесених при потужності 100 Вт, підтверджують потенційне електричне застосування плівок NbN, нанесених методом розпилення при постійному струмі.

**Ключові слова:** Плівка NbN, Вплив потужності, Структурний, Корозія, Електричні характеристики.