Effect of deposition time on tribological and adhesion characteristics of niobium nitride thin films

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Abstract. Nitrides are, in general, refractory materials that are used in a wide range of applications such as hard coatings, cutting tools, insulators, microelectronics, and diffusion barriers and so on. The aim of this study is to deposit niobium nitride thin films and to characterize them by atomic force microscopy and X-ray diffraction analyses. The niobium nitride thin films were deposited by direct current magnetron sputtering on silicon Si (100) substrates. Some deposition parameters such as the discharge current, the argon and the nitrogen flow rates, deposition temperature and the pressure inside the chamber were kept constant. The deposition process was carried out at different times, namely 10, 20, 30 and 40 minutes respectively. Atomic force microscopy investigations were performed on the so-deposited films to characterize them from the adhesion and tribological point of view at nanoscale and thus, to emphasize the influence of the deposition time on these characteristics. The results highlighted a significant influence of the deposition time on both adhesion and tribological properties of the investigated niobium nitride thin films.

1. Introduction

Niobium nitride is known to have some mechanical, tribological, chemical and physical properties that recommend it for applications in different industries [1-3]. It is characterized by a high melting point, good mechanical and superconducting properties, thermal stability, and so on [4-6]. Besides their use as hard, protective and decorative coatings in wear applications, niobium nitride can also be used in detector applications, nano-structured X-ray detectors, superconducting electronics, Josephson junctions, diffusion barriers etc. [2, 7-10]. Direct current (DC) or radio frequency (RF) magnetron sputtering [8, 11, 12], cathodic arc deposition [1, 3], atomic layer deposition [4], pulsed laser deposition [10, 13] are often used for depositing niobium nitride thin films on different substrates. The deposition parameters such as deposition time, nitrogen flow rate, deposition temperature, and pressure are impacting greatly the characteristics of the films. Niobium nitride (NbNx) can crystallize in cubic (δ-NbN), tetragonal (γ-Nb4N3) or hexagonal (η-NbN, ε-NbN, β-Nb2N) phases [14, 15]. In general, the structure of the films can consist of more than one single NbNx phase. Each of the existing phases is changing the mechanical and tribological properties of the films.

This paper is a research on niobium nitride thin films deposited by DC magnetron sputtering on silicon substrates at different deposition times. It aims at revealing the influence of the deposition time on the tribological and adhesion characteristics of the investigated thin films at nano scale.
2. Materials and experimental procedure
The obtaining of niobium nitride thin films was done using a niobium target with a purity of 99.95 %. The films were deposited by DC magnetron sputtering on silicon Si (100) substrates. A reactive sputtering facility from the Materials Science and Engineering, Technical University of Cluj-Napoca was employed. The base pressure inside the deposition chamber was 10^-7 torr. For starters, the silicon substrates were cleaned in an ultrasonic bath with acetone and isopropyl alcohol and blown with compressed air. The atmosphere consisted of an argon and nitrogen mixture. The pressure was about 2 mtorr and the discharge current was of 350 mA. The argon flow rate was 40 cm^3·min^-1 while the nitrogen flow rate was 1.5 cm^3·min^-1. The distance between the niobium target and the silicon substrates was of 60 mm. The deposition process was done at four different deposition times namely 10, 20, 30 and 40 minutes. A JEOL 560LV scanning electron microscope was used for determining the thickness of the deposited films. The films deposited for 10 minutes had a thickness of 0.18 µm, those deposited for 20 minutes 0.35 µm while the thickness of the films deposited at 30 and 40 minutes was 0.53 and 0.70 µm respectively.

The so-deposited niobium nitride thin films 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. The tests were performed in the contact mode of the AFM, at room temperature for a relative humidity of 25 %. The dimensions of the PPP-NCHR cantilever used in testing – according to the manufacturer – are: resonance frequency: 400 kHz, force constant: 42 N·m^-1, thickness: 4 µm, width: 30 µm, length: 125 µm. The tip radius is smaller than 10 nm and its height was of 15 µm. XRD (X-ray diffraction) analyses were performed using a Inel Equinox 3000 diffractometer using a cobalt radiation (λ₁=1.7889 Å, λ₂=1.7928 Å). The 2-theta angle was ranged between 25 and 100 °.

3. Theoretical formula
The friction force that occurs when the AFM tip and the surface of the samples are in contact can be determined based on the tip deflection, Δz, which is recorded in the scanning process (Figure 1). This parameter, F_f, can be calculated using the equation (1) [16]. R is a constant (r = 0.33), G represents silicon shear modulus (G = 50.92·10^3 N·µm^-2) and h, b, l, and s are the cantilever dimensions that are mentioned above.

\[ F_f = \frac{(r \cdot \Delta z \cdot G \cdot h^2 \cdot b)}{(l^2 \cdot s)} \]  

(1)

![Image of the XEI software for determining the cantilever deflection of a niobium nitride thin films deposited 20 minutes.](image1.png)

4. Results and discussion
Atomic force microscopy analyses were performed on the deposited films to determine their topographical, tribological and adhesion characteristics. All the samples were scanned in five different areas and the roughness parameters were obtained using the XEI Image Processing Tools for SPM (Scanning Probe Microscope) Data (Figure 2).
The average roughness and the maximum height of the profile are two of the topographical parameters of interest. The average values determined for the mentioned parameters of the investigated niobium nitride thin films are given in Table 1. A strictly increasing trend with the increase in deposition time was observed for both topographical parameters. The average roughness has increased from 0.13 up to 0.89 nm when the deposition time was increased from 10 to 40 minutes.

Table 1. Average roughness, $R_a$, and the average maximum height of the profile, $R_z$, of the deposited niobium nitride thin films.

| Deposition time (min) | $R_a$ (nm) | $R_z$ (nm) |
|-----------------------|------------|------------|
| 10                    | 0.13       | 2.47       |
| 20                    | 0.33       | 3.44       |
| 30                    | 0.68       | 6.28       |
| 40                    | 0.89       | 8.97       |

The friction force was calculated based on tip deflection (see section 3). The fluctuation of the friction force dependent on the deposition time is graphically given in Figure 3. Analysing the average values, we can conclude that the friction force is decreasing continuously with the increase in deposition time. Its values have varied between 52 and 90 nN and it has fluctuated inversely proportional to the roughness. It is found that the friction force might increase slowly first and only afterwards it starts decreasing when the deposition time is ranged between 10 and 20 minutes. Instead, the increase in deposition time from 30 to 40 minutes can be accompanied by a decrease followed by an increase in friction force.
Figure 3. Friction force fluctuation in terms of deposition time for niobium nitride thin films

The adhesion, which is the main failure mechanism in MEMS (microelectromechanical systems) devices, was investigated by spectroscopy-in-point mode of the AFM. After performing such tests, force vs. Z scan curves of the type shown in Figure 4 are recorded. The interpretation of this curves with the XEI Image Processing Tools for SPM Data gives us information about the adhesion force (pull-off force), attractive force (snap-in force) and the adhesion energy. The red curve corresponds to the loading stage while the blue curve corresponds to the unloading stage.

Figure 4. Adhesion characteristics determined by spectroscopy in point for a niobium nitride thin film deposited for 30 minutes.

Figure 5 presents the fluctuation of the adhesion in terms of deposition time for the investigated niobium nitride thin films. First an increase in adhesion force was marked out when the deposition time was increased from 10 to 30 minutes. The increase was more pronounced between 10 and 20 minutes (it varied from 135 to 215 nN) after which it had increased slightly (up to 225 nN). Instead the
increase in deposition time from 30 to 40 minutes led to a significant decrease of the adhesion force (to about 115 nN).

Figure 5. Adhesion force of niobium nitride thin films in respect to deposition time.

We assume that the change in both tribological and adhesion properties is due to existence in these films of different phases [14, 15]. The XRD analyses had pointed out that the Nb$_2$N phase was obtained in the case of the films deposited for 40 minutes. This phase was not observed on the films deposited for deposition time smaller than 40 minutes. We will not rule out the possibility that the Nb$_2$N phase also exist in the other films if its quantity is too small to be detected by the diffractometer.

Figure 6. XRD patterns for the niobium nitride thin films deposited for 30 and 40 minutes.

5. Conclusions
Niobium nitride thin films were deposited on silicon substrates at different deposition time. The increase in deposition time from 10 to 40 minutes was accompanied by the increase in average roughness. The friction force varied inversely proportional to the roughness parameter, constantly decreasing. The adhesion force has increased first with the increase in deposition time up to 30
minutes after which it decreased suddenly. The change in tribological and adhesion characteristics can be attributed to the presence of different phases in the microstructure of the investigated niobium nitride thin films. Further research will aim at determining the surface energy of these films and to investigate the influence of relative humidity on the tribological and adhesion characteristics.

6. References
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