STRUCTURAL ANALYSIS OF NbN THIN FILMS GROWN THROUGH RF MAGNETRON SPUTTERING

ANÁLISIS ESTRUCTURAL DE PELÍCULAS DELGADAS DE NbN CRECIDAS A TRAVÉS DE PULVERIZACIÓN CATÓDICA MAGNETRÓN RF

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ABSTRACT

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In this work NbN thin films have been grown through rf magnetron sputtering technique from a δ-NbN (99.99%) target. In particular, we have studied the influence of the additional N2 flux in the preparation chamber in crystallization and microstructure of the deposited films. The films have been characterized by X-Ray diffraction (XRD) in θ-2θ configuration and at grazing angle, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD results show that the films grown at different fluxes of N2 have high textured coefficient along [200] direction. SEM results indicate the films have columnar growth with high homogeneity and average thickness of 0.7 μm. TEM results reveals that the films have grown from crystalline nanoparticles of NbN with highly textured along the (200) plane.

Keywords: Thin films, grazing angle, crystalline structure, nanoparticles.

RESUMEN

En este trabajo se han crecido películas delgadas de NbN a través de la técnica de pulverización catódica magnetrón rf a partir de un blanco de δ-NbN (99,99%). En particular, se ha estudiado la influencia que tiene la incorporación de flujo adicional de N2 a la cámara de preparación en la cristalización y la microestructura de las películas depositadas. Las películas se han caracterizado por difracción de rayos X (DRX) en la configuración de θ-2θ y en ángulo de incidencia rasante, microscopía electrónica de barrido (SEM) y microscopía electrónica de transmisión (TEM). Los resultados de DRX muestran que las películas crecidas en diferentes flujos de N2 tienen alto coeficiente de textura a lo largo de la dirección [200]. Los resultados de SEM indican

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que las películas tienen un crecimiento columnar con alta homogeneidad y espesor medio de 0,7 μm. Los resultados de TEM revelan que las películas han crecido a partir de nanopartículas cristalinas de NbN con alta textura a lo largo del plano (200).

Palabras clave: Películas delgadas, ángulo rasante, estructura cristalina, nanoparticulas.

1. Introduction

Transition metal nitrides have physics and chemical properties such as high fusion points and chemical stability that allow it be used in different applications spanning from hard coatings to electromagnetic radiation detectors. For instance, the NbN films have been studied as potentially useful material for low temperature electronics, because the highest transition temperature is of approximately 17.3 K, value that allows to be used in fabrication of multilayer films of (NbN/AlN/NbN) type which have been used as tunnel junctions [1, 2]. Likewise, due their value of work function (4.7 eV) there is the possibility of using NbN as cathode in vacuum microelectronic devices [3]. Other nitrides such as TiN and TaN have been used as diffusion barriers to prevent copper diffusion into silicon used in microelectronic devices.

Although NbN has been prepared as thin films using different techniques including reactive phase rf magnetron sputtering [4, 5], pulsed laser deposition (PLD), or atomic layer deposition [6], influence of some deposit fabrication parameters such as argon pressure in the work chamber or the power supplied to the target on the structural properties of the deposited materials have not been studied. This work presents results obtained from the growth of NbN thin films on glass substrates, through rf magnetron sputtering technique which has proven to be quite versatile to prepare a variety of different materials [7]. In particular, we have studied the crystalline structure, microstructure and morphology of the NbN films deposited with different nitrogen fluxes.

2. Experimental techniques

The equipment used to grow the NbN films is an Alcatel HS 2000 rf magnetron described in previous papers [8]. The NbN films were obtained from a 4"x1/4" NbN (99.9%) target (CERAC, Inc.). The parameters used during deposition process were: base pressure 2.0×10^{-4} Pa, total working pressure 7×10^{-1} Pa, deposition time 30 min, target–substrate distance 5 cm and argon (99.999%) flux in 20 standard cubic centimeters per minute (sccm). We studied the influence of additional nitrogen (99.99%) flux inside the deposit chamber ($\Phi = 2$, $\Phi = 4$, and $\Phi = 6$ sccm) in the structural and microstructure of the films. The final working pressure was maintained using a valve controller for all the nitrogen flow values given above, the argon and nitrogen flows were controlled by mass flow controllers.

The structural characterization of the films was performed by X-ray diffraction (XRD) with a Philips diffractometer operated at 30 kV and 20 mA and using Cu Kα radiation. Surface morphology was characterized by imaging the secondary electrons with a FEI-Quanta 2000 scanning electron microscope operating at 15 kV and 10 mA filament current. Microstructure characterization was carried out with 2100F and FEI-Titan 80-300 transmission electron microscope, both equipped with energy-dispersive X-ray spectroscopy detector (EDXS).

The samples analyzed by TEM were prepared according to the following procedure: two samples with rectangle shape (4x5 mm) were cut, these two rectangles were glued with epoxy resin, cross section slices were obtained using an ultrasonic cut, the slices were fixed in a brass tube (3 mm diameter) and further disks were cut, the disks were thinned with sandpaper and disks with abrasive (40, 15 and 4 μm grain-size), final thinned sample was obtained with a dimple and the finally step was ion beam milling using Ar ions at 5 keV.

3. Results and discussion

Fig. 1a shows the Rietveld analysis carried out in the target used to growth the NbN thin films. The study established that the crystalline phase of the target is δ-NbN (a= 4.3927Å) face centered-cubic (SG Fm-3m). The fig. 1b shows the difference between the experimental and calculated XRD patterns.

In a previous work we found that the optimal conditions to deposit NbN thin films were: 300 W of power supply to the target and heating the substrate to 553 K [9]. In order to study the influence of gas addition on the structural and morphology properties of the NbN films we have introduced nitrogen gas in the deposition chamber. XRD studies of these films have previously been performed and are detailed elsewhere [9], in brief it was shown that in all cases a preferential growth appears along the (200) plane (see Fig. 2) and the polycrystalline character of the film was established by X-ray diffraction experiments at grazing incidence (see Fig. 3). These results indicate that incorporation of nitrogen du-

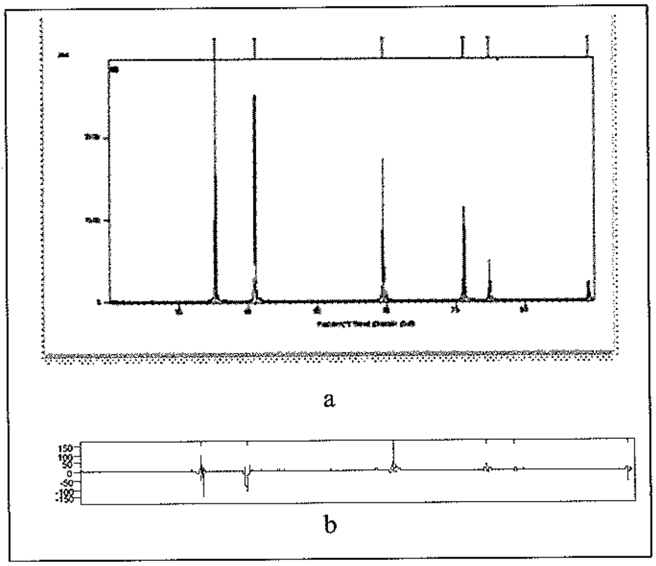

Figure 1 a- Experimental XRD pattern and calculated of NbN target and b- difference of the two patterns.

ring the growth of the films determined the direction of the δ-NbN phase, this is evidencing by texture coefficient (defined as $[\Gamma_{(200)} = I_{(200)}/ [I_{(200)} + I_{(111)} + I_{(220)} + I_{(311)} + I_{(222)}]$ where I is the intensity of diffraction peak) which was of 0.65 to the films grown at 6 sccm.

Moreover, previous works on the growth of NbN thin films by different techniques (sputtering, cathodic arc, and reactive methods) [10, 11] have established that the variation in texture may depend on factors such as the treatment of the substrate prior coating, the deposition rate [6] the type of substrate and the highly non-equilibrium condition of the plasma sputtering [12]. Furthermore, Bendavid *et al.* [13] showed that the substrate bias voltage also affects the microstructure and preferred orientation. Also it has been shown that changing the nitrogen flow during the growth of TiN films interchanges the preferred orientation of the films from the [111] direction to the [200] direction, it is due to incorporation of nitrogen during the deposition process that implies changes in the dynamics of the plasma since the increase in the number of nitrogen molecules increases the probability of collisions, promoting a larger number of chemical reactions on the substrate surface. Consequently, the presence of the nitrogen atoms reduces the flux of cations from the (200) to the (111) planes, resulting in the orientation of the growth in the [200] direction [14].

The surface morphology of these films have previously been characterized [9], showing that the grown NbN films present a compact granular structure, with a columnar growth of the type described by Movchan and. Demchishin [15] having an average thickness of 0.7 μm (see Fig. 4).

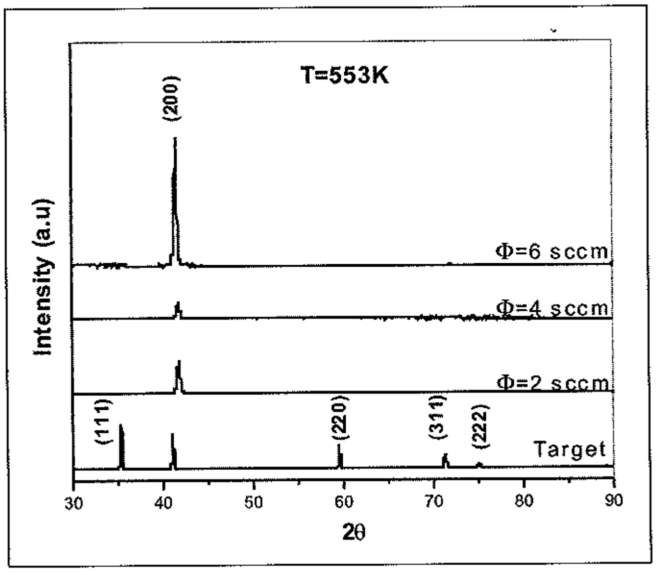

Figure 2. XRD patterns recorded from NbN films deposited at 553 K, 300 W and with different nitrogen fluxes. The pattern of the target from which the films were obtained is included for comparison purposes. Published with permission number 3157800386723 of JMS.

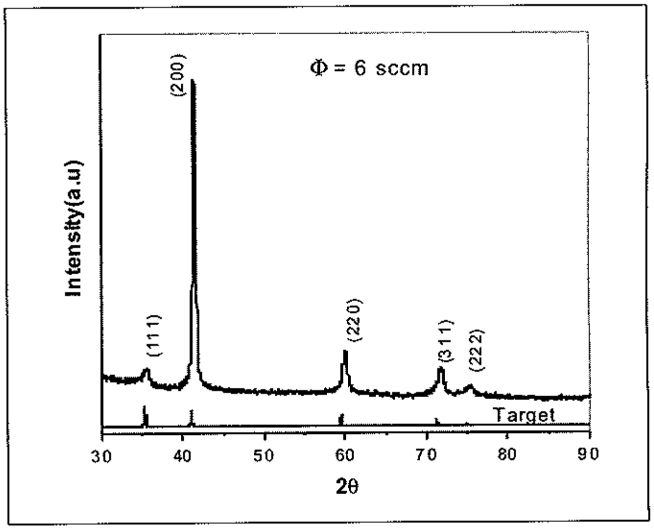

Figure 3. Grazing angle (2°) XRD pattern recorded from a NbN film grown at 553 K, 300 W, and 6 sccm nitrogen flux. The target XRD pattern is included as reference. Published with permission number 3157800386723 of JMS.

The structural analysis of the NbN films was completed by transmission electron microcopy (TEM) through the electron diffraction patterns (DP) measurements and high resolution

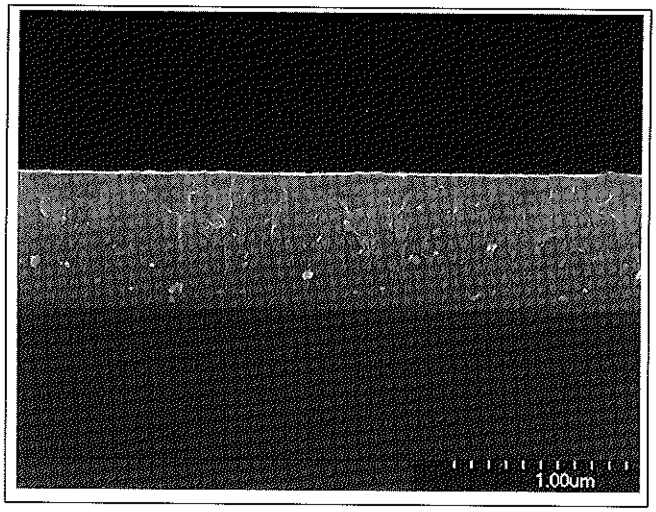

Figure 4. Cross-section SEM micrograph obtained with secondary electrons of the NbN film grown at 300 W, 513 K and 6sccm nitrogen flux. Published with permission number 3157800386723 of JMS.

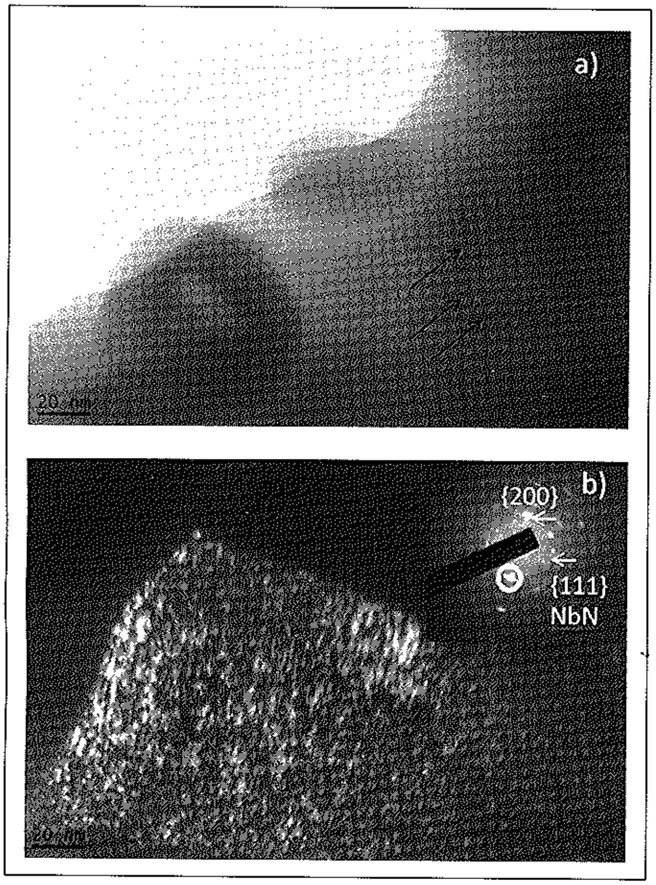

Figure 5. a) Bright field image of the film grown at 2 sccm nitrogen flux and b) dark field imageof the film grown at 6 sccm, with the corresponding electron diffraction pattern.

images (HRTEM) obtained from the films which were grown at 2 and 6 sccm of nitrogen flux. Fig. 5a corresponds to the bright field image of the film grown at 2sccm and Fig. 5b shows the dark -field image of the film which was grown in a high flux (6 sccm). Where, it can be seen that the film is formed by concentrated clusters of nanoparticles with dimension less than 10 nm and that the films grown at 6 sccm have a nanostructured morphology and grew mainly along of {111} and {200} family planes.

TEM analysis was also performed to analyze the NbN films morphology as a function of nitrogen flux, Fig. 6a and 6b show the morphology of the NbN films grown at 2 sccm and 6 sccm nitrogen fluxes, respectively. Micrographs reveal films are nano structured and that there are constituted by clusters and amorphous regions. All the samples are formed by nanograins homogenously distributed. The size of clusters was in the 2 nm to 10 nm range. It was observed that the amount of NbN clusters increases as the nitrogen flux increases too. Using Gatan software we have determined that the average grain size of the nanoparticles was 2.7 ± 0.6 nm with normal distribution. HRTEM image (Fig. 6c) presents an interferential pattern produced by the atomic planes and its corresponding Fourier transform, lets us visualize the re-

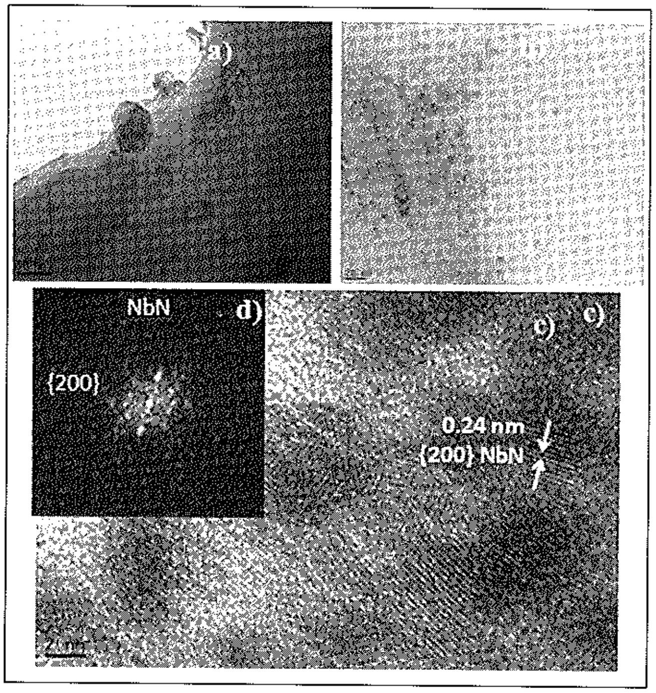

Figure 6. TEM images showing NbN nanoparticles with spherical morphology at different nitrogen fluxes: a) 2 sccm; b) 6 sccm; c) HRTEM image, NbN nanograins growing in a preferential direction of atomic planes (200) can be observed in d.

ciprocal space of one NbN nanoparticle (Fig. 6d). Measuring the distance between the spots (0.24 nm), we can confirm that they correspond to the (200) planes of δ-NbN. These results are in agreement with XRD analysis, which established that NbN grows preferentially along the (200) plane. The physical explanation of the phenomena that produces the preferential growth along the (200) plane of NbN has been given in a previous work [9].

Finally, EDX analysis (Fig. 7) confirms that the analyzed clusters were constituted by Niobium and Nitrogen. Si, Al, Ba, Fe, O correspond to the elements of the common glass substrate. Presence of copper is due to the sample holder.

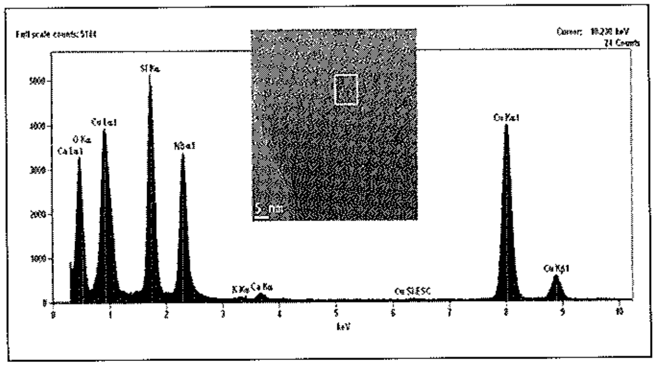

Figure 7. EDX spectrum of NbN films grown at 6 sccm of nitrogen flux.

Conclusions

The results obtained in this work indicate that during the preparation of NbN films by rf magnetron sputtering, the variation of nitrogen flux introduced in the preparation chamber has decisive influence on the orientation and morphology of the deposited films, since that as a function of the nitrogen flux, these grow with high texture coefficient along the [200] direction and the morphology evolves from nanometric clusters to nanoparticles homogeneously distributed.

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