Electrical analysis of niobium oxide thin films

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ABSTRACT

In this work, a series of niobium oxide thin films was deposited by reactive magnetron sputtering. The total pressure of Ar/O_2 was kept constant at 1 Pa, while the O_2 partial pressure was varied up to 0.2 Pa. The depositions were performed in a grounded and non-intentionally heated substrate, resulting in as-deposited amorphous thin films. Raman spectroscopy confirmed the absence of crystallinity. Dielectric measurements as a function of frequency (40 Hz–110 MHz) and temperature (100 K–360 K) were performed.
The dielectric constant for the film samples with thickness (d) lower than 650 nm decreases with the decrease of d. The same behaviour was observed for the conductivity. These results show a dependence of the dielectric permittivity with the thin film thickness. The electrical behaviour was also related with the oxygen partial pressure, whose increment promotes an increase of the Nb_2O_5 stoichiometry units.

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1. Introduction

In nature, niobium is one of the most abundant metals on the earth crust. It oxidizes in air at temperatures above 200 °C. The most common oxidation states are 2 + (NbO), 4 + (NbO_2) and 5 + (Nb_2O_5). NbO is a metallic material which exhibits superconductivity at 1.38 K and has been used as a resistor in superconducting circuits. NbO_2 is a semiconductor with exceptional field-switching properties and has been analysed to have a reducing agent for fuel cell technology.

Nb_2O_5 has the highest chemical stability among all, being one of the useful optical materials due to its good corrosion resistance in both acid and base media, high refractive index (2.4 at 550 nm), low absorption and a high transparency in the UV–Vis–NIR region. It is an n-type semiconductor with a wide band gap of about 3.4 eV ([1,2] and [3]). Nb_2O_5 can be in the amorphous state or in one of several different crystalline polymorphs. In general all the physical properties of Nb_2O_5 depend on its polymorphy. From the amorphous phase it crystallizes in the hexagonal phase when heat-treated (HT) at temperatures between 300 and 600 °C, in the orthorhombic phase (HT between 700 and 1000 °C) and in the monoclinical phase (HT > 1100 °C) ([1,2] and [3]). This pentoxide is a transparent dielectric material which makes it ideal for capacitor technology, due to its high dielectric constant (~41 at room temperature and 10 MHz), as well as for the use in optical systems, for example in intelligent windows, solar cells and it is a potential electrochromic material that can offer different colours like brown, gray, green or blue. It is also used, as a component, in the production of ferroelectric devices ([4–7] and [8]). It must be noticed that when the Nb_2O_5 is mixed, in the appropriate amounts, with alkali metal oxides, niobate perovskites with interesting electric properties are formed, as for example $LiNbO_3$, $NaNbO_3$, and $KNbO_3$. These niobates, when embedded in glass matrixes are materials with high potential for electro-optic applications ([9–13] and [14]).

The traditional preparation methods of oxides matrixes [15] often present problems of stoichiometry due to oxygen deficiency. Moreover, the presence of contaminants and/or defects in the networks can give origin to electronic states, which modify the desired conductivity due to the incorporation of donors or acceptors and also deep electronic states that capture the charge carriers (the presence of interstices, gaps and surface states also affect the conduction mechanisms). Reactive magnetron sputtering leads to high purity thin films, with the possibility to control the amount of oxygen in the final product, modifying the properties of the thin film [16,17].

Nowadays, the microelectronic industry demands the miniaturization of components which implies the study of materials presenting equal or similar electrical, thermal and optical responses when compared to those used, but significantly improving their dimensions. The dielectric properties of niobium pentoxide enhances its application in ultra small electrical capacitors. The analysis of this physical property was the motivation of the present work where we report the results on the preparation of amorphous niobium oxide thin films, by reactive magnetron sputter deposition and the analysis of the dielectric properties as a function of the oxygen partial pressure and film thickness. In this study, the growth of niobium oxide in the amorphous form was intentional. The preparation parameters that allow the formation of amorphous Nb_2O_5, enhancing the dielectric properties, were studied. The

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heat-treatment of this late Nb_2O_5 amorphous film will allow to a control the growth of thin films with different Nb_2O_5 crystalline polymorphs. This late study is not the focus of the present work.

2. Experimental details

2.1. Film deposition

The thin films were produced by DC reactive magnetron sputtering. A stainless steel vacuum chamber was pumped down to a base pressure lower than 6×10^{-4} Pa. The argon and the oxygen flow were controlled with mass flow controllers. The gas pressure during sputtering was measured with a capacitance gauge, while the residual gas pressure was measured with a Penning gauge. The total working pressure (argon pressure plus oxygen pressure) was kept constant at 1 Pa for all the depositions.

Metallic Nb target, with 5 cm in diameter and 3 mm in thickness and with a purity of 99.95% (Kurt Lesker) was clamped to a conventional DC magnetron and powered by a DC supply unit (Huttinger), designed for magnetron sputtering.

The thin films were deposited on conductive Si <111> substrates doped with boron (resistivity ~0.001 Ω cm), which were previously dipped in HF. The main function of this chemical treatment was the elimination of any SiO_2 layer that could exist in the surface of the substrate. The target–substrate distance was kept constant at 12 cm, the discharge current 0.7 A and the deposition time 15 min, for each sample. The samples were named in accordance with the O_2 molar fraction used during their preparation.

2.2. Structural and morphological characterizations

The thickness of the thin films was measured using a Taylor-Hobson Talystep. Chemical composition was obtained using an electron probe microanalyser (EPMA) JEOL (JXA-8621MX, current beam 30 nA, voltage 15 kV) by averaging 9 points distributed over the sample surface. Crystallinity was evaluated by X-ray diffraction (XRD — CuKα radiation, λ = 1.54056 Å) θ/2θ with a LynxEye Silicon Strip detector mounted into a D8 discover apparatus (Bruker axs).

The structural characterization of the samples was complemented with Raman spectroscopy, performed at room temperature, in a back-scattering geometry with a 325 nm line of a He-Cd laser. A microscope objective (50×) focused the exciting light onto the sample (spot diameter <0.8 μm). The plasma lines were removed by a filter.

2.3. Electrical and dielectric measurements

For the electrical measurements the low resistivity substrate worked has bottom electrode and silver conductive paint was used to produce the top electrode. Thus, parallel plate capacitor geometry was obtained. During the measurements, the samples were maintained in a helium atmosphere in order to improve the heat transfer and eliminate the moisture. The dc electrical conductivity (σdc) was measured using a Keithley electrometer, model 617, as a function of the temperature (100–360 K). The impedance spectroscopy measurements were performed in the frequency range of 40 Hz–2 MHz using an Agilent 4294A LCR, in the Cp-Rp configuration, as a function of the temperature (100–360 K). The permittivity was then calculated using Eq. 1.

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = C_P \frac{d}{\varepsilon_0 A} - j\frac{d}{\omega R_P \varepsilon_0 A} \qquad (1)$$

Where Cp and Rp represent the measured capacitance and resistance, d is the sample thickness, A is the top electrode area and ε_0 is the permittivity of the empty space (8.8542×10^{-12} F/m).

A quantitative characterization of the dielectric measurements was made by fitting the frequency dependent permittivity data with the
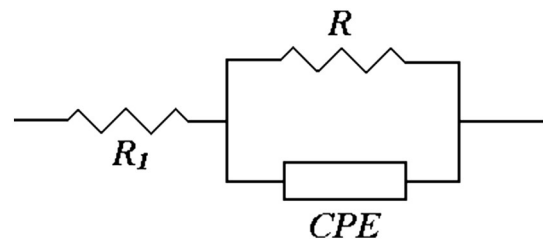

Fig. 1. Equivalent electrical circuit.

values calculated from an equivalent circuit, characterized by resistance R1 in series with the parallel between a resistance (R) and a constant phase element (CPE) ([17,18] and [19]). Fig. 1 represents this electrical circuit. In the ε″ versus ε′ representation, the interception of the ε′ axis at high frequency, is R1 that was considered in this fitting process equal to 1 Ω. The impedance of this intuitive element (CPE) can be defined by Eq. 2:

$$1/Z_{CPE} = Q(j\omega)^n \qquad (2)$$

where Q ([Q] = Fsn-1) and n (0 ≤ n ≤ 1) are adjustable parameters. The Q and n parameters are independent of the frequency ([17] and [18]). The algorithm calculates R, Q and n parameters which best fits the measured data. For this fitting procedure, WinFit software, from Novocontrol, was used.

3. Results and discussion

Table 1 links the oxygen partial pressure to the chemical composition and thickness of the thin films. Fig. 2 shows the XRD and Raman spectra of all the samples, which present an amorphous nature. However it is observed that with the increase of the O_2 molar fraction, a phase change occurs. This change is associated with the decrease in the intensity of the broad band centred at ~34° and the increase of the broad band centred at ~53° (Fig. 2.a). This transition can be related with the increase in the Raman spectra of the 640 cm^{-1} vibration band (Fig. 2.b), which is characteristic of NbO_6 octahedral vibrations of the Nb_2O_5 amorphous structure ([3,15] and [20]). Therefore, the increase of the oxygen partial pressure promotes an increase of the Nb_2O_5 amorphous units. The Raman band at 960 cm^{-1} is related to symmetric stretching of terminal Nb=O bonds on the surface, due to highly distorted NbO_6 octahedra ([3,15,20] and [21]). The shoulder at 490 cm^{-1} is assigned to vibrations of Nb–O bonds, in slightly distorted NbO_6 octahedra [21] and the large band at ~300 cm^{-1}, which intensity increases with the increase of the oxygen partial pressure, is assigned to Nb–O–Nb vibrations [3]. The presence of very-low intensity diffraction peaks, in the XRD spectrum of the thinnest films (thickness below 500 nm (Table 1)), are assigned to the substrate.

The dc conductivity measurements showed that σdc (Fig. 3) tends to increase, in all the samples, with increasing temperature. It was noticed that electrical conductivity decreases with the oxygen partial pressure, probably due to the increase of Nb_2O_5 species, which have non-metallic characteristics. This hypothesis is corroborated by the fact that the dc activation energy, calculated by applying the Arrhenius equation in the

Table 1
Relation between O_2 mole fraction, oxygen to Niobium CONTENT and thickness of the different studied samples. All thin films were sputtered during 15 min.

PO$_2$/P total	O/Nb	Thickness [μm]
3	1.5	1.0
7	1.6	1.1
11	1.9	0.6
15	1.8	0.5
20	1.8	0.4