



The crystallization and properties of sputter deposited lithium niobite



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ABSTRACT

Sputter deposition of the thin film memristor material, lithium niobite (LiNbO_2) is performed by co-deposition from a lithium oxide (Li_2O) and a niobium target. Crystalline films that are textured about the (101) orientation are produced under room temperature conditions. This material displays memristive hysteresis and exhibits XPS spectra similar to MBE and bulk grown LiNbO_2 . Various deposition parameters were investigated resulting in variations in the deposition rate, film crystallinity, oxygen to niobium ratio, and mean niobium oxidation state. The results of this study allow for the routine production of large area LiNbO_2 films at low substrate temperature useful in hybrid-integration of memristor, optical, and energy storage applications.

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1. Introduction

Lithium niobite (LiNbO_2) is a sub-oxide of the more common acoustic and optical wave-guiding material lithium niobate (LiNbO_3). Lithium niobite is a mixed ion-electron conductor that has been explored for battery [1] and neuromorphic [2] applications. It is a layered [3] semiconductor [1] with loosely bound lithium ions [4,5]. Deintercalation of the lithium ions, forming Li_xNbO_2 ($0 < x < 1$), yields a degenerately doped p-type [6,7] material with a high density of states at the Fermi energy [7–9]. Modulation of the lithium content by chemical [1], electrical [10], or optical [11] means creates opportunities for multi-functional devices based on the resulting memristive [12,13] and optical changes [1,3,11]. Additionally, a low temperature superconducting transition was found for lithium deintercalated material (Li_xNbO_2) [14] despite the band structure similarities to high temperature cuprate superconductors [6,7].

Early work on lithium niobite was performed on powdered material that likely contained unreacted precursors [3] or other impurities [9] leading to discrepancies in experimental measurements such as both metallic [7] and semiconducting [1] temperature dependent resistivity as well as diamagnetic [4], paramagnetic [1,14], and antiferromagnetic [3] behavior. Such discrepancies have been previously noted in the literature [7,9]. Later work was performed on single crystal material in bulk form grown by liquid phase electro-epitaxy with a molten salt solution [7,15] and in thin films grown by molecular beam epitaxy using a metal-chloride chemistry [2,16]. While both of these methods for growing single crystalline lithium niobite involve high temperature corrosive environments, herein we report a method for sputter deposition of lithium

niobite using traditional vacuum technologies common in industrial microfabrication and facilitating integration with other semiconductor technologies for advanced functionality.

2. Experimental setup

All sputter depositions reported herein were performed on a modified Denton Discovery 18 sputtering system with three confocal sputtering cathodes, an electrically isolated platen that can be heated above 800 °C, and controlled flows of Ar, O₂, and N₂ process gases. The system was pumped to a base pressure of 3×10^{-7} Torr using a turbo pump and a cryo pump. During deposition the pressure was controlled using a constant gas flow and a variable conduction throttle valve on the turbo pump. Argon was chosen for the working gas and no reactive species were introduced.

This work explores 1 h co-depositions from an RF energized lithium oxide (Li_2O) target and a DC energized niobium target on to c-plane sapphire substrates. The sputtering targets measure 3.625 in. in diameter and are indium bonded directly to the water cooling blocks for improved heat transfer. The platen was water cooled to remove excess heat produced by the sputtering process.

The physical properties of the deposited films were analyzed using X-ray diffraction (XRD) and cross sectional scanning electron microscopy (SEM). XRD was performed with a Panalytical X-ray diffractometer using Cu K-alpha radiation. Cross sectional SEM was performed on a Hitachi SU8230 electron microscope to determine the film thickness. Cross sectional samples were prepared by tensile fracture.

XRD 2θ - Ω scans were performed between 10 and 80° in order to determine the crystallinity of the deposited film and identify phases. The crystallinity of the film was determined from the XRD peak height scaled by the sapphire substrate peak height and the film thickness.

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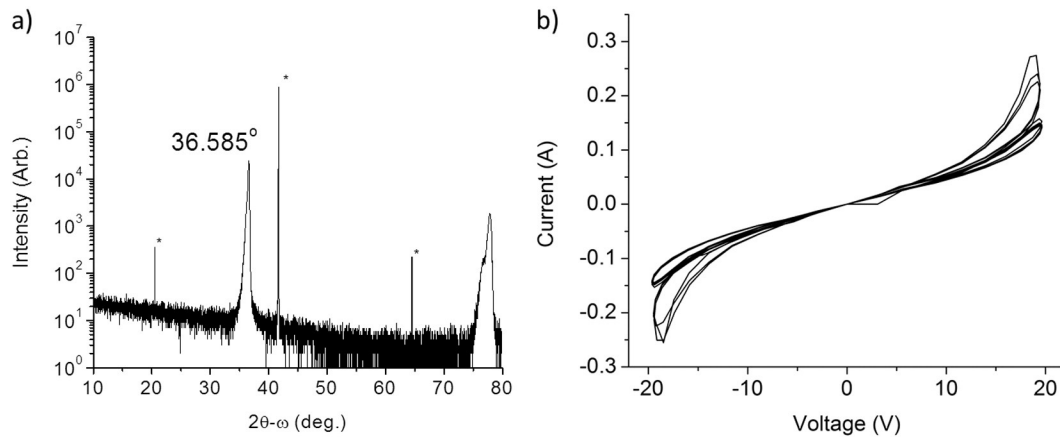


Fig. 1. (a) X-ray diffractogram for the initial deposition condition showing a single strong peak at 36.585° corresponding to (101) oriented lithium niobite. (b) Current–voltage curves measured from the sputter deposited material with Ti/Au contacts. These curves exhibit memristive hysteresis similar to previously reported lithium niobite devices.

All of the deposited films produced an XRD peak $2\theta-\Omega = 36.39^\circ\text{--}36.87^\circ$ corresponding to the XRD peak for the (101) orientation of LiNbO_2 . The location of this peak can vary due to strain and variations in lithium or oxygen content. Changes in lithium content, Li_xNbO_2 where $0.5 < x < 1$, change the hexagonal lattice spacing between $a = 2.900\text{--}2.925 \text{ \AA}$ and $c = 10.46\text{--}10.465 \text{ \AA}$ [1]. This range of unstrained lattice constants results in a range of XRD angles $2\theta-\Omega = 36.48^\circ\text{--}36.77^\circ$.

In addition to variations in the (101) oriented Li_xNbO_2 XRD peak location, alternative phases with notable XRD peaks near this range make exact phase identification difficult via XRD alone. Other phases with XRD peaks near the measured peaks include Nb_{FCC} (111) at 36.77° , NbO (111) at 36.95° , LiNb_3O_8 (600) at 36.99° , and Li_3NbO_4 (222) at 36.99° . Thus, multiple experimental methods must be utilized to conclusively prove or disprove the films as LiNbO_2 such as electrical device measurements or chemical composition measurements.

The chemical composition of the deposited films was analyzed using X-ray photoelectron spectroscopy (XPS). In addition to the chemical composition, the oxidation state of the niobium atoms was determined by shifts in the niobium 3d signal at a binding energy between 200 and 215 eV. While the chemical composition of niobium and oxygen can be easily determined by XPS, lithium has only a single XPS peak at a binding energy of 54.9 eV which unfortunately overlaps with the niobium 4s signal at 55.6 eV. This makes quantization of lithium content via XPS difficult.

The oxygen to niobium ratio was determined by dividing the total area under the O 1s peak by the area under the Nb 3d peak. Each area

was scaled by known relative sensitivity factors for these peaks, which are 2.4 for niobium and 0.66 for oxygen [17]. The niobium oxidation state reported herein is a weighted mean value calculated, according to Eq. (1), from fitting the niobium XPS spectra.

$$\text{Mean oxidation} = \frac{\sum_{n=0}^{n=5} n * \text{Peak area}(n)}{\sum_{n=0}^{n=5} \text{Peak area}(n)} \quad (1)$$

where n is the integer oxidation states of niobium (0–5) used to fit the measured XPS spectrum. These integer oxidation states exhibit doublets in XPS with known binding energies that shift to higher energy as niobium becomes oxidized [18]. All oxygen to niobium ratios and niobium oxidation states reported herein are measured from XPS spectra after argon milling into the film. This procedure avoids sample to sample variations in surface oxide formation, but results in lower reported oxygen to niobium ratios than the actual film composition due to preferential sputtering removing more oxygen than niobium [19].

3. Results and discussion

An initial coarse study of deposition conditions was performed varying the niobium target power, lithium oxide target power, operating pressure, and substrate temperature over a wide range of deposition conditions. Many of these films resulted in Li–Nb–O phases not useful in memristive devices. From this wide variation of deposition conditions, a

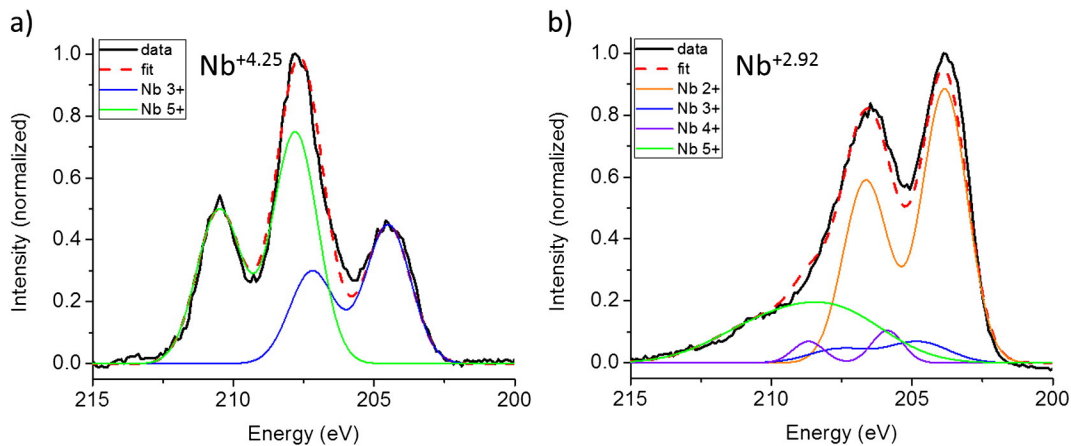


Fig. 2. (a) Niobium XPS spectrum measured from the surface of the initial deposition condition film. This spectrum can be fit using only the 3+ and 5+ oxidation states. (b) Niobium XPS spectrum after milling into the initial deposition condition film. The data requires a broad range of oxidation states in order to fit the spectrum and has a lower mean oxidation state than the surface measurement due to preferential sputtering of the oxygen during milling.

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