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.

Keywords

Lithium Niobite; Sputter Deposition; X-ray Diffraction, X-ray Photoelectron Spectroscopy

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.

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 hour co-depositions from an RF energized lithium oxide (Li₂O) target and a DC energized niobium target on to c-plane sapphire substrates. The sputtering targets measure 3.625 inches 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 – 80 degrees 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. All of the deposited films produced an XRD peak between 2θ - ω = 36.39° – 36.87° corresponding to the XRD peak for the (101) orientation of LiNbO₂. The location of this peak can vary due to strain and variations in lithium or oxygen content. Changes in lithium content, Li_xNbO₂ where 0.5 < x < 1, change the hexagonal lattice spacing between a = 2.900 – 2.925 Å and c = 10.46 – 10.465 Å [1]. This range of unstrained lattice constants results in a range of XRD angles between 2θ - ω = 36.48° – 36.77°.

In addition to variations in the (101) oriented Li_xNbO₂ 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°, LiNb₃O₈ (600) at 36.99°, and Li₃NbO₄ (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 – 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 Equation 1, from fitting the niobium XPS spectra.

$$\text{Mean Oxidation} = \frac{\sum_{n=0}^{n=5} n * \text{PeakArea}(n)}{\sum_{n=0}^{n=5} \text{PeakArea}(n)} \quad \text{Equation 1}$$

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].

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 deposition condition that resulted in $\text{Li}_x\text{NbO}_{2-y}$ was observed. This condition became the central deposition condition about which this study's parameters were varied.

Central Deposition Condition

The central deposition condition found from the coarse optimization was $P_{\text{Nb}} = 50$ W, $P_{\text{Li}_2\text{O}} = 200$ W, Pressure = 1 mTorr, and Temperature = Unheated ($\approx 30^\circ\text{C}$). These conditions were found to produce crystalline material with a strong XRD peak at 36.585°

consistent with (101) oriented LiNbO_{2-x} and also exhibited memristive hysteresis, as shown in Figure 1, when measured under conditions identical to previous LiNbO_2 devices [20]. Thus, this material behaves similar to LiNbO_2 produced by MBE [2] or LPEE [20].

Figure 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.

The XPS spectra for this central deposition condition are shown in Figure 2 where Figure 2a was measured from the film's surface and Figure 2b was measured after milling into the film. The surface spectra can be fit using only the Nb^{3+} and Nb^{5+} oxidation states. The ratio of the areas of these two peaks weighted by the oxidation state yields a mean oxidation state of 4.25 as shown in Figure 2a. In contrast, the existence of a surface oxide and preferential sputtering during the XPS depth profile causes a lower mean oxidation state of 2.92 after milling into the film. Preferential sputtering during the depth profile removes more oxygen than niobium and causes a mixture of many oxidation states [19] as shown in Figure 2b. While this ambiguity in absolute oxidation state determination prevents quantization of the exact oxidation state, comparisons from one sample to another allow relative changes in oxidation state to be determined.

Figure 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.

In order to compare the sputter deposited films to a known LiNbO_2 standard, XPS of bulk LiNbO_2 , grown by liquid phase electro-epitaxy [15], was performed. As shown in Figure 3, the niobium XPS spectrum for the sputter deposited film is nearly identical to the XPS spectrum for the bulk grown material indicating that the sputtered material has a chemical environment around the niobium atoms that is similar to the previously characterized [15] bulk grown material.

Figure 3: XPS spectra for the sputtered initial deposition condition and for bulk grown lithium niobite. These two spectra match closely indicating similar chemical environments around the niobium atom in these two materials.

In order to investigate the effects of various deposition parameters on the physical and chemical properties of the deposited film, niobium target power, lithium oxide target power, operating pressure, and substrate temperature were varied around the central deposition conditions.

Niobium Power

The niobium target power was varied between 30 W and 150 W. Over this range, the thickness of the deposited material increases nearly linearly as the niobium target power is increased at a rate of 5.6 nm/W, as shown in Figure 4a. In addition, the crystallinity of the film, measured by XRD intensity, increases rapidly for low niobium target powers and decreases slowly for higher niobium power, which may occur due to chemical changes in the film's deposited with more niobium. Chemically, as shown in Figure 4b, the niobium oxidation state decreases as the niobium target power increases. This is consistent with adding more niobium to the film and making the film more metal rich. The oxygen to niobium ratio also decreases as the niobium target power increases, although the film deposited with 40 W niobium power is an outlier from this trend. These chemical trends indicate a narrow niobium power range of 40 – 50 W wherein the desired Li_xNbO_2 films are obtained. This region also corresponds with the best XRD figures of merit as shown in figure 4a.

Figure 4: (a) Physical trends in changing niobium target power showing an increase in film thickness as the niobium target power increases and a peak in crystallinity as measured by XRD intensity. (b) Chemical trends in changing niobium target power showing a generally decreasing trend in both niobium oxidation state and oxygen to niobium ratio as the niobium target power increases.

Lithium Oxide Power

The lithium oxide (Li_2O) target power was varied between 100 W and 300 W. Over this range, the thickness of the deposited material increases as the Li_2O target power is increased in a nearly linear manner at a rate of 1.55 nm/W, as shown in Figure 5a. Unlike the range of niobium target powers investigated, the film crystallinity decreases throughout the entire range of Li_2O target power. Not surprisingly, increasing the Li_2O target power increases the oxidation state in the deposited film. This is consistent with adding more oxygen to the film. However, the measured oxygen to niobium ratio does not track with the niobium oxidation state and is mostly unchanged by changing the Li_2O target power.

Figure 5: (a) Physical trends in changing Li_2O target power showing an increase in film thickness as the Li_2O target power increases. Unlike the range of niobium target powers investigated, the film crystallinity decreases over the range of Li_2O target powers investigated. (b) Chemical trends

in changing Li₂O target power showing a generally increasing trend in niobium oxidation state and mostly constant oxygen to niobium ratio as the Li₂O target power increases.

Pressure

The operating pressure was varied between 1 mTorr and 30 mTorr. Over this pressure range the mean free path of an atom should vary between 20 cm and 0.7 cm respectively according to the kinetic model for gas collisions shown in Equation 2.

$$\Gamma = \frac{k_B T}{\pi d^2 P} \quad \text{Equation 2}$$

where Γ is the mean free path, k_B is Boltzmann's constant, T is temperature, d is the diameter of an atom (Argon assumed), and P is pressure. The range of mean free paths investigated extends both longer and shorter than the 10 cm target to substrate distance spanning cases from molecular to viscous flow which result in dramatically different energetic species impinging on the substrates.

Increasing the pressure between 1 – 10 mTorr had little impact on the thickness of the deposited film, although the film crystallinity decreased over this range, as shown in Figure 6a. The decrease in film crystallinity may be due to increased scattering as the mean free path becomes shorter than the target to substrate distance. In sputter deposition, unscattered atoms carry a large amount of kinetic energy, typically 4 – 40 eV [21], which can provide the energy necessary for crystallization. The films deposited at pressures between 1 – 10 mTorr show only small changes to the niobium oxidation state and oxygen to niobium ratio.

However, the film deposited at 30 mTorr is approximately 1/3 the thickness of the films deposited at lower pressures and exhibits an oxygen to niobium ratio approximately 2.5 times higher than the films deposited at lower pressure despite a relatively unchanging niobium oxidation state. Since the oxygen to niobium ratio increased without increasing the niobium oxidation state, excess lithium must be incorporated into the film and while we cannot measure Li-O bonding with XPS, such bonding must exist. The film deposited at 30 mTorr also exhibits a higher crystallinity than the low pressure trend would predict which may be due to the change in chemical composition.

Figure 6: (a) Physical trends in changing pressure showing a relatively unchanging film thickness between 1 – 10 mTorr with decreasing crystallinity and a film approximately 1/3 the thickness at 30 mTorr (b) Chemical trends in changing pressure showing small increases in the niobium oxidation state and oxygen to niobium ratio at pressures between 1 – 10 mTorr and a substantially higher oxygen to niobium ratio at 30 mTorr.

Substrate Temperature

The substrate temperature was varied between room temperature and 800°C. Unintentional heating of the substrate at room temperature was controlled by water cooling the platen. The measured temperature did not exceed 40°C for the unintentionally heated films. As shown in Figure 7, increasing the substrate temperature to 500 °C had little effect on the film thickness, crystallinity, niobium oxidation state, or oxygen to niobium ratio. However, increasing the substrate temperature to 800 °C caused a decrease in the film thickness and crystallinity. The film deposited at 800 °C also exhibited a higher niobium oxidation state and higher oxygen to niobium ratio. In addition to the quantitative chemical measurements, the film deposited at 800 °C was transparent as opposed to the opaque films deposited at lower temperatures. The XRD peak for the 800 °C sample was also located at a slightly higher angle ($2\theta - \omega = 36.87^\circ$) than all other films investigated in this study ($2\theta - \omega = 36.39^\circ - 36.76^\circ$). Of the known Li-Nb-O compounds with XRD peaks near $2\theta - \omega = 36^\circ - 37^\circ$, Li_3NbO_4 and LiNb_3O_8 are the only transparent compounds, with a band gap of approximately 4 eV [22, 23], having a higher ideal niobium oxidation state of Nb^{5+} , and a higher angle XRD peak than all other compounds in this range. Thus, the 800 °C sample is likely dominated by Li_3NbO_4 or LiNb_3O_8 .

Figure 7: (a) Physical trends in changing substrate temperature showing a small decrease in film thickness and crystallinity between 30 – 500 °C and a larger decrease in both film thickness and crystallinity at 800 °C (b) Chemical trends in changing substrate temperatures showing small increases in the niobium oxidation state and oxygen to niobium ratio between 30 – 500 °C and a larger increase in niobium oxidation state and oxygen to niobium ratio at 800 °C.

Excess Lithium

It may be noted that no linear combination of Li_2O and Nb can form LiNbO_2 . In order to obtain the ideal 2:1 oxygen to niobium ratio, excess lithium must a) not incorporate into the deposited film or b) evolve out of the film after it has been deposited. All of the films examined herein, with the exception of the film deposited at 800 °C, reacted with air upon removal from the sputtering chamber to form an insulating film on top of the deposited film, as shown in Figure 8. Examining the XPS spectra for lithium, niobium, and oxygen, shown in Figure 9, the surface layer is composed of lithium and oxygen with no niobium present. After milling into the deposited film, niobium and oxygen are both present. Lithium may also be present after milling, but the lithium 1s spectrum overlaps the niobium 4s spectrum making its quantization indeterminate. It can also be noted from the XPS spectra in Figure 9 that the oxygen binding energy shifts from the surface region to the bulk of the film, which indicates that the oxygen is bound differently on the surface and after milling. This suggests two distinctly different films as shown in the cross sectional SEM in Figure 8. The surface

layer that forms is water soluble and upon dissolution turns deionized water basic, pH of 10 – 11 in 100 mL of water, likely due to the formation of LiOH.

Figure 8: Cross sectional SEM of a sputter deposited film showing a layer on top of the deposited film. This layer forms after deposition due to a reaction with the air and is water soluble.

Figure 9: (a – c) XPS spectra for lithium, niobium, and oxygen of the reacted surface layer and after milling through to the main deposited film. The surface layer is composed of lithium and oxygen with no niobium present. The main film contains at least niobium and oxygen, but the lithium XPS signal is washed out by the niobium 4s signal.

Conclusion

We have demonstrated the room temperature deposition of thin film crystalline lithium niobite (LiNbO_2) with a (101) orientation by co-sputtering from a lithium oxide (Li_2O) target and a niobium target along with a systematic method to optimize its deposition. This material displays memristive hysteresis and exhibits XPS spectra similar to MBE and bulk grown LiNbO_2 . The effects of various deposition parameters were investigated including niobium target power, lithium oxide target power, operating pressure, and substrate pressure. Maintaining low pressure and temperature improved the deposition rate and film crystallinity without significantly impacting the film's chemical properties. Increasing the niobium or lithium oxide target powers resulted in increased deposition rates. However, changing the target powers also changed the chemical composition of the deposited film resulting in a narrow window in which memristive LiNbO_2 can be achieved. Thus, sputter deposition can be tailored to result in LiNbO_2 useful in memristive applications even for near ambient conditions, potentially useful in hybrid integration of memristors with other computational or optical systems.

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Figure 1

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Figure 6

Figure 7

Figure 8

Figure 9