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# Molecular Beam Epitaxy of lithium niobium oxide multifunctional materials

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#### ABSTRACT

The role of stoichiometry and growth temperature in the preferential nucleation of material phases in the Li-Nb-O family are explored yielding an empirical growth phase diagram. It is shown that while single parameter variation often produces multi-phase films, combining substrate temperature control with the previously published lithium flux limited growth allows the repeatable growth of high quality single crystalline films of many different oxide phases. Higher temperatures (800–1050 °C) than normally used in MBE were necessary to achieve high quality materials. At these temperatures the desorption of surface species is shown to play an important role in film composition. Using this method single phase films of NbO, NbO<sub>2</sub>, LiNbO<sub>2</sub>, Li<sub>3</sub>NbO<sub>4</sub>, LiNbO<sub>3</sub>, and LiNb<sub>3</sub>O<sub>8</sub> have been achieved in the same growth system, all on c-plane sapphire. Finally, the future of these films in functional oxide heterostructures is briefly discussed.

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#### 1. Introduction

The lithium niobium oxide family consists of conducting, semiconducting, and insulating materials across a wide resistivity and bandgap range. Fig. 1 lists the resistivity of a few materials in the system as a function of niobium valence, ranging from conducting niobium to insulating lithium niobite (LiNbO<sub>3</sub>). These materials span 22 orders of magnitude in resistivity with bandgaps from IR to UV [1–8]. Oxides in general have many desirable multifunctional properties, for example; piezoelectric, pyroelectric, and ferroelectric effects which can exist in a single material such as lithium niobate [9,10]. Lithium niobite (LiNbO<sub>2</sub>), a suboxide of the same family, is currently the focus of multiple research areas. LiNbO<sub>2</sub> is used as a memristor for neuromorphic applications, a battery cathode material showing potential for high rate capability and long term cycle stability, and is also studied for unique optical properties [11–13]. NbO<sub>2</sub> acts as a digital memristor, a device with discrete on and off resistance states. NbO2 is currently used in memory, neuristor circuitry, and relaxation oscillator circuitry [14–16]. The Li-Nb-O material family also includes other ceramics of various dielectric constants used in a variety of applications including battery electrodes, microwave frequency dielectrics, phosphors, photocatalysts for water reduction, and hysteretic MIM tunnel diodes or "memdiodes" (Li<sub>3</sub>NbO<sub>4</sub>, LiNb<sub>3</sub>O<sub>8</sub>, and Nb<sub>2</sub>O<sub>5</sub>) [17–22,5,23,24].

The growth optimization of these materials in a single deposition system is desirable due to the variety of properties that can be achieved and the potential heterostructure devices that can be imagined. Among these possibilities are strain enhanced sensors and MEMS, high K dielectrics, tunable dielectrics, superlattices, thin film batteries, memtransistors, multi-layer neuromorphic heterostructures, and ferroelectric switching transistors with switchable enhanced channel conductance [25,26]. Despite the potential for new and enhanced functional devices

and materials, this Li-Nb-O multifunctional material family remains relatively unexplored. A many-phased oxide system inherently contains significant complexity. The phase diagram of the Li<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub> system is complicated by multiple phases existing in a very small range of temperature and stoichiometry [27]. Due to these tight tolerances, precise control and understanding of all parameters is necessary for controllable growth of heterostructures and single phase materials. Molecular Beam Epitaxy (MBE) is an excellent platform for high stoichiometry control and crystalline quality, and therefore a good candidate for controlled growth of these materials [25]. The MBE growth of Li-Nb-O materials using NbCl<sub>5</sub> as a high vapor pressure niobium precursor has been previously described by a lithium controlled niobium incorporation rate method [28]. Briefly, NbCl<sub>5</sub> can be reduced to elemental niobium in the presence of lithium and a hot substrate where lithium getters the chlorine. LiCl desorbs due to its high vapor pressure leaving elemental niobium to react with oxygen and excess lithium. In the same work a method of single parameter phase control in the Li-Nb-O system is described where the lithium







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**Fig. 1.** (Lithium) Niobium oxides plotted by their resistivity versus niobium valence, spanning 22 orders of magnitude resistivity. Materials can be conducting, semiconducting, or insulating depending on the oxidation state. The insulators  $Li_2O$ ,  $Li_3NbO_4$ , and  $LiNb_3O_8$  are omitted for clarity.

supply is limited while niobium and oxygen are supplied in excess. The lithium flux directly controls the amount of adsorbed niobium so that adjusting the Li flux modifies niobium to oxygen ratio, and therefore the oxidation state, with respect to the constant  $O_2$ . This study was performed at a single substrate temperature, 900 °C, and in practice often produces multiple phases laterally across a film due to temperature gradients across the surface at high temperature growths. In this work it is shown substrate temperature plays a role in the preferential nucleation of various phases in the Li-Nb-O family, and that by combining this new understanding with the above lithium controlled niobium incorporation rate method single phase films spanning the entire phase space can be epitaxially grown.

#### 2. Experiment

#### 2.1. Growth system modifications

The materials in this work are grown in a Varian Gen-II style MBE system which has been customized for the growth of lithium niobium oxides using a lithium assisted metal-halide growth chemistry discussed in detail by Henderson et al. [28]. The method involves the sublimation of NbCl<sub>5</sub> from a custom water and filament heated near-ambient cell, described elsewhere, allowing controllable evaporation of high vapor pressure materials (typical bulk operating temperatures are 35–50 °C) [29].

A modified Veeco corrosive series antimony cracker with a custom solid tantalum crucible is used to supply lithium to the system where it getters chlorine from NbCl<sub>5</sub> and HCl. Excess lithium may be incorporated into the film, and along with the niobium in the presence of oxygen can form a variety of phases in the lithiumniobium-oxygen phase system such as LiNbO<sub>2</sub>, LiNbO<sub>3</sub>, Li<sub>3</sub>NbO<sub>4</sub>, and LiNb<sub>3</sub>O<sub>8</sub>. The phase which is grown depends on the Li:NbCl<sub>5</sub> flux ratio, the supplied oxygen, and the substrate temperature as will be shown in this work.

A custom Vesco-NM substrate heater is used to allow growth at high temperatures in a corrosive oxygen and chlorine environment. The heater consists of a thick tantalum filament fully encased in PBN, which can be heated to 1000 °C in an oxygen background of  $5 \times 10^{-5}$  torr.

#### 2.2. Substrate preparation

All films in this work are grown on c-plane (006) oriented sapphire substrates. The substrates are cleaned by acetone, methanol, and isopropyl alcohol followed by 4:1 H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> at 120 °C before loading and degassing in a separate chamber, being careful during loading to minimize sample contact with the surrounding metal substrate holder which will conduct thermal energy away from the sample creating thermal non-uniformity.

#### 2.3. Characterization

Films were structurally characterized by a Phillips Xpert MRD diffraction system using Cu-K<sub> $\alpha$ </sub> X-rays ( $\lambda$  = 1.54056 Å). Phase identification of lithium niobium oxides by X-ray diffraction (XRD) is challenging due to the existence of multiple phases with similar crystal structures. There are five possible phases in the narrow range 36.772–37.069° 20- $\omega$ , and 3 of those materials fall within 0.4° of each other, making phase identification extremely difficult. It is possible to differentiate them all, however, using multiple XRD scans as well as knowledge of the material in question. In this work film transparency, the existence of double or half X-ray reflections, and asymmetric diffraction scans are analyzed together to definitively identify material phases [30]. The surface morphology of the films was characterized by a Veeco atomic force microscopy (AFM) system.

#### 3. Results and discussion

#### 3.1. Growth parameters

Previous work in Li–NbCl<sub>5</sub>–O<sub>2</sub> growth chemistry indicated that phase control was best mediated by a lithium controlled niobium incorporation rate approach. Because the niobium supply is controlled by lithium, the niobium to oxygen ratio can be adjusted by varying a single parameter, the Li flux. It was shown that through this method increasing the Li flux produced films of reduced oxidation state, resulting in a progression from Li<sub>3</sub>NbO<sub>4</sub>  $\rightarrow$  LiNbO<sub>3</sub>  $\rightarrow$  LiNbO<sub>2</sub>  $\rightarrow$  NbO as the Li flux is increased holding all other fluxes constant at constant substrate temperature [28].

Motivated by the prevalence of multi-phase films, temperature studies were carried out to analyze the effect of substrate temperature on the nucleation of various phases. Fig. 2 shows the X-ray diffractograms of films grown at constant flux while substrate temperature is increased from 925 to 1000 °C in steps of 25°. For these growths the beam equivalent pressures as measured by Bayard-Alpert ion flux gauge were approximately  $6 \times 10^{-7}$  torr for Li and



**Fig. 2.** X-ray diffractograms of films grown at increasing substrate temperature while holding all fluxes constant ( $\phi = 0.6$ ). From bottom to top in 25° increments, 925 °C primarily produces Li<sub>3</sub>NbO<sub>4</sub>, 950 and 975 °C primarily produces LiNbO<sub>2</sub> and 1000 °C primarily produces LiNbO<sub>3</sub>. All films are multi-phase. The temperature dependence is attributed to increased Li desorption.

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