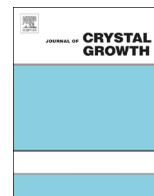




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# Molecular beam epitaxy growth of niobium oxides by solid/liquid state oxygen source and lithium assisted metal-halide chemistry



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## ABSTRACT

In order to consistently grow high quality niobium oxides and lithium niobium oxides, a novel solid/liquid state oxygen source,  $\text{LiClO}_4$ , has been implemented in a molecular beam epitaxy (MBE) system.  $\text{LiClO}_4$  is shown to decompose into both molecular and atomic oxygen upon heating. This allows oxidation rates similar to that of molecular oxygen but at a reduced overall beam flux, quantified by in situ Auger analysis.  $\text{LiClO}_4$  operation is decomposition limited to less than 400 °C, and other material limitations are identified. The design of a custom near-ambient  $\text{NbCl}_5$  effusion cell is presented, which improves both short and long term stability. Films of Nb oxidation state +2, +3, and +5 are grown using these new tools, including the multi-functional sub-oxide  $\text{LiNbO}_2$ .

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## 1. Introduction

Transition metal oxides have enabled and improved many technologies such as hydrogen production, methane production, photocatalysis, resistive ram, and memristors [1–3]. Often novel material properties are made possible by the d-orbital electrons found in transition metals such as niobium, which allow for various bonding mechanisms and oxidation states. In particular, several stable niobium oxides exist with different niobium to oxygen ratios due to the various niobium oxidation states. Examples include a  $\text{Nb}^{2+}$  semimetal ( $\text{NbO}$ ) [4], a  $\text{Nb}^{4+}$  semiconductor ( $\text{NbO}_2$ ) [5], and a  $\text{Nb}^{5+}$  insulator ( $\text{Nb}_2\text{O}_5$ ) [6]. Lithium bearing niobium oxide ternaries exhibit optical waveguiding and ferro/piezoelectric properties in lithium niobate ( $\text{LiNbO}_3$ ,  $\text{Nb}^{5+}$ ) [7–9] while the sub-oxide lithium niobite ( $\text{LiNbO}_2$ ,  $\text{Nb}^{3+}$ ) has memristive [10] and low  $T_c$  superconducting properties [11], as well as applications as a battery cathode material [12].

Many properties such as ferromagnetism, piezoelectricity, and pyroelectricity rely on single crystalline material of the highest quality in order to maximize their effect, and many multi-functional devices have been realized by perovskite materials, heterojunctions, and superlattices such as  $\text{BiFeO}_3$  and  $\text{BiTiO}_3/\text{SrTiO}_3$  [13,14]. It is therefore desirable to develop a method for growing high quality metal oxide films of varying metal oxidation state to exploit these multi-functional properties.

Molecular beam epitaxy (MBE) provides monolayer control and high quality material. However, the growth of stoichiometric refractory metal oxides by molecular beam epitaxy (MBE) is traditionally difficult because of inadequate oxygen and low vapor pressure metal sources leading to extremely low growth rates [15]. Transition metals are difficult to evaporate controllably due to high temperature requirements and the poor compatibility of a hot electron beam filament with an oxygen environment.  $\text{LiNbO}_3$  is very difficult to grow stoichiometric in oxygen, and it is often annealed post-growth to incorporate the correct amount of oxygen in the film [16]. It is difficult for any niobium film to reach full oxidation in an MBE environment at the high growth temperatures required for quality single crystalline material, and therefore a more reactive oxidizer is desirable to reach these fully oxidized states. Previous work has explored oxidizers such as oxygen plasmas and dangerous ozone sources [17]. This work investigates a solid/liquid state oxygen source as an alternative to these gas based methods, as well as a new style of MBE effusion cell for the evaporation of metal-halide sources which offer much lower evaporation temperatures and therefore greater flux stability [18].

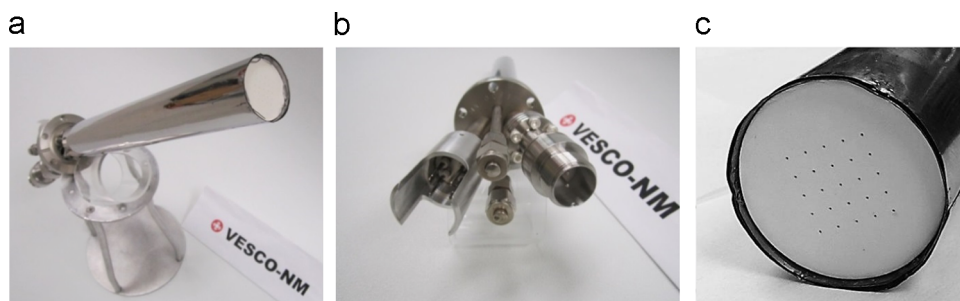
## 2. Experimental methods

### 2.1. Custom cell design

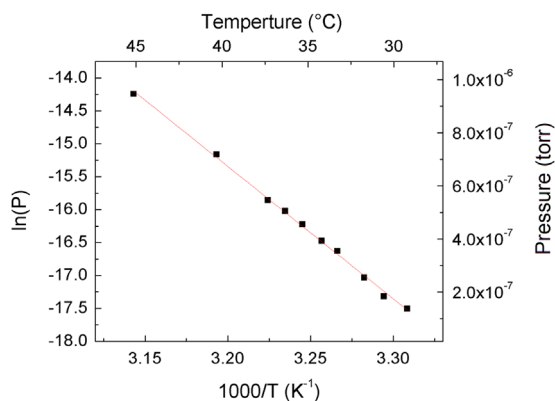
Historically, refractory metals have been evaporated by electron beam to achieve growth level fluxes in MBE; however, the hot filament used to create the electron beam oxidizes and breaks easily in an oxide growth environment. For this reason, niobium

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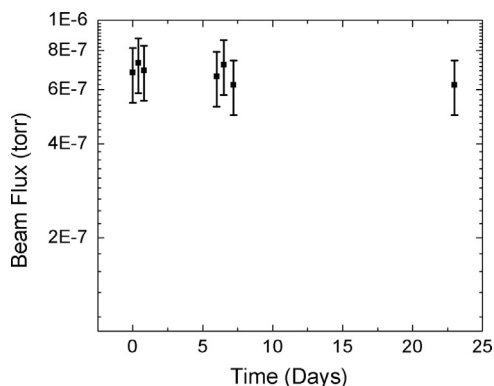
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**Fig. 1.** (a) Custom NbCl<sub>5</sub> cell with (b) tip filament, bulk water, tip and bulk thermocouple feedthroughs, and (c) a 5 × 5 hole pattern aperture plate.



**Fig. 2.** The measured NbCl<sub>5</sub> flux (BEP) versus temperature on an Arrhenius plot follows an expected linear trend. Growth level fluxes occur above ~30 °C. The included fit gives an equation  $\ln(P) = 49.0 - 20.1 (1000/T(K))$ .



**Fig. 3.** Measured NbCl<sub>5</sub> flux at a single setpoint over a period of 24 days. The cell remains stable within the error range (20%) of a standard ion flux gauge, depicted by error bars ( $\sigma = 4.39 \times 10^{-8}$  Torr).

oxides have been previously deposited using a lithium assisted metal-halide growth chemistry [10,16,18]. In this method the niobium source is NbCl<sub>5</sub>, present as the dimer Nb<sub>2</sub>Cl<sub>10</sub>, which has an equilibrium vapor pressure of  $\sim 1 \times 10^{-4}$  Torr at 20 °C. The chlorine from NbCl<sub>5</sub> is getterd by lithium forming LiCl that desorbs from the substrate surface at growth level temperatures (vapor pressure=3.61 Torr at 900 °C). This growth method is described in depth by Doolittle et al. [16], Greenlee et al. [10] and Henderson et al. [18]. In this previous work, the material was evaporated from a Createc NATC-40-40-290 oil/water heated cell, which provided temperature stability of  $\sim 0.1\%$ . Despite this stability, radiation from the hot substrate ( $\sim 900$  °C) caused the NbCl<sub>5</sub> cell temperature to rise, increasing the growth rate gradually over the course of the growth.

To overcome this problem, a custom evaporation cell was designed featuring two zone heating and an aperture plate. The

cell, shown in Fig. 1, was manufactured by VESCO-NM. The bulk material zone of the cell is, like the former case, temperature controlled by an oil or water bath to maintain stable temperatures in the near-ambient range. A second heating zone was added at the tip of the cell, heated by a traditional filament that along with a PBN aperture plate provides thermal isolation from the substrate radiation. The hot zone also prevents condensation on the aperture plate and allows a back pressure of NbCl<sub>5</sub> for more stable flux control. The crucible is an 82 cm<sup>3</sup> elongated quartz tube, which is filled half full of material to avoid evaporation from the hot zone.

The vapor flux from the new cell design, measured in beam equivalent pressure (BEP), follows a linear trend with temperature on an Arrhenius plot, shown in Fig. 2, as is expected for Knudson flow. Growth level NbCl<sub>5</sub> fluxes can be achieved at 30–60 °C compared to previous work at 25–35 °C, indicating flow retardation by the aperture plate. After 6 months of use, the aperture plate shows no corrosion or clogging, indicating the hot zone operating temperature of 100–150 °C is sufficient to prevent any condensation. The cell was measured for long term flux stability over a period of 24 days, shown in Fig. 3, and shows stability within the quoted error range of a standard ion flux gauge (20% within a pressure decade), indicating that flux drift is reasonably controlled with this design.

## 2.2. Lithium perchlorate

Previous work has indicated that oxygen incorporation into a niobium oxide films at high temperatures ( $> 650$  °C) is difficult, with the fully oxidized state of niobium (chemical valence +5) difficult to achieve. LiNbO<sub>3</sub> films have been grown by MBE in the past, as well as the ceramics Li<sub>3</sub>NbO<sub>4</sub> and LiNb<sub>3</sub>O<sub>8</sub>, but the repeatability of these growths is poor due in part to low and variable oxygen incorporation [16]. This oxygen incorporation issue has led to the use of a stronger oxidizer than molecular oxygen, lithium perchlorate (LiClO<sub>4</sub>), as an alternative to a higher reactivity sources such as ozone and oxygen plasmas which require a very specific flow control and in the case of the former extensive safety regulation due to reactivity. Lithium perchlorate has the highest volumetric density of oxygen of any material, including liquid oxygen, and is the only material in the perchlorate family that is stable above its melting point [19]. The material is traditionally used as a chemical oxygen generator for emergency oxygen candles as well as a method of chemical oxygen storage [19,20]. Lithium perchlorate is also highly soluble in a number of solvents and is used in this form as a soluble electrolyte for lithium ion batteries.

Lithium perchlorate exists in the solid state as salt granules at room temperature. The substance melts at 236 °C in its anhydrous form, although it is highly hygroscopic and must be handled in a dry environment. Once hydrated, its melting point shifts to  $\sim 247$  °C. Lithium perchlorate begins to decompose near 400 °C, with the reaction becoming exothermic around 420 °C [19,21,22]. The material decomposes according to the following equations:

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