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MOCVD Deposition of Epitaxial $LiNbO_3$ Thin Films Using the Single-Source Precursor $LiNb(OEt)_6$

Alex A. Wernberg* and Henry J. Gysling

Corporate Research Laboratories,
Eastman Kodak Company
Rochester, New York 14650-2111

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Lithium niobate, $LiNbO_3$, is an electrooptic ceramic that has applications in devices such as couplers, switches, modulators, deflectors, and rf spectrum analyzers.[1] In addition, the nonlinear optical properties and large electrooptic and piezoelectric coefficients of $LiNbO_3$ make it a useful material for integrated optic applications.[1g,h] Thin films of this perovskite material have been fabricated by thermal evaporation,[2] magnetron and rf sputtering,[3] liquid-phase epitaxy,[4] molecular beam epitaxy,[5] and laser ablation.[6] Solution coating methods have also been used to fabricate $LiNbO_3$ films (i.e., sol–gel processes using ethanol solutions of $LiNb(OEt)_6$,[7] and a metalorganic decomposition process using $Li[Nb(OPh)_6]$ and $Li[NbL_3]$, L = catecholato, pinacolato[8]). Although metalorganic chemical vapor deposition (MOCVD) has a number of advantages as a commercial thin-film fabrication process (e.g., high deposition rate, multiwafer capacity, large area deposition, and ability to give conformal coverage), little work has been reported using this technique for $LiNbO_3$ films. This is probably due to the lack of suitable volatile precursor reagents for deposition of this complex oxide. Unlike materials such as GaAs and ZnS, which can be readily deposited by dual source MOCVD processes in the presence of excess group V or VI reagents, respectively, the many thermodynamically stable phases possible for complex oxides of Li and Nb require precise control of reagent stoichiometries for the deposition of the desired $LiNbO_3$ phase. Thus, for oxides such as lithium niobate, single-source precursors with the desired stoichiometry of the metals may offer significant advantages in composition control as well as simplified processing. Prior to our work only one report had described the fabrication of $LiNbO_3$ films using a MOCVD process (i.e., a two-source process using lithium 2,2,6,6-tetramethylheptane-3,5-dionate (Lidpm) and $Nb(OMe)_5$).[9] Films reported in this earlier work[9] were polycrystalline and black as deposited, making them unsuitable for optical applications. We have recently reported that epitaxial $LiNbO_3$ films can be deposited by a spray MOCVD process using a toluene solution of a single-source precursor generated in situ by the reaction of $Nb(OEt)_5$ and Lidpm.[10] Although these films were epitaxially oriented with respect to the substrate, their rough surface morphology made them unsuitable for device applications.

In this communication we report the fabrication of epitaxial $LiNbO_3$ thin films of improved crystalline properties and surface morphology using the well-characterized single-source reagent, $LiNb(OEt)_6$.[11] The spray MOCVD film fabrication technique used for these depositions is essentially a chemical vapor deposition process in which precursors with relatively low vapor pressure are transported via a mist into a hot-wall reactor where rapid and efficient volatilization occurs. Previous work in our laboratory has demonstrated its utility for the fabrication of high-quality thin films of various semiconductors (i.e., ZnS,[12] GaAs,[13] InSe,[14] and In_2Se_3[14]) using single-source precursor reagents. A related MOCVD process (supercritical fluid-transport chemical vapor deposition), which can also use precursors of low volatility, has been recently reported.[15]

$LiNb(OEt)_6$, a white, crystalline solid, was prepared by the reaction of $Nb(OEt)_5$ with LiOEt (generated in situ by the addition of a stoichiometric amount of lithium wire to

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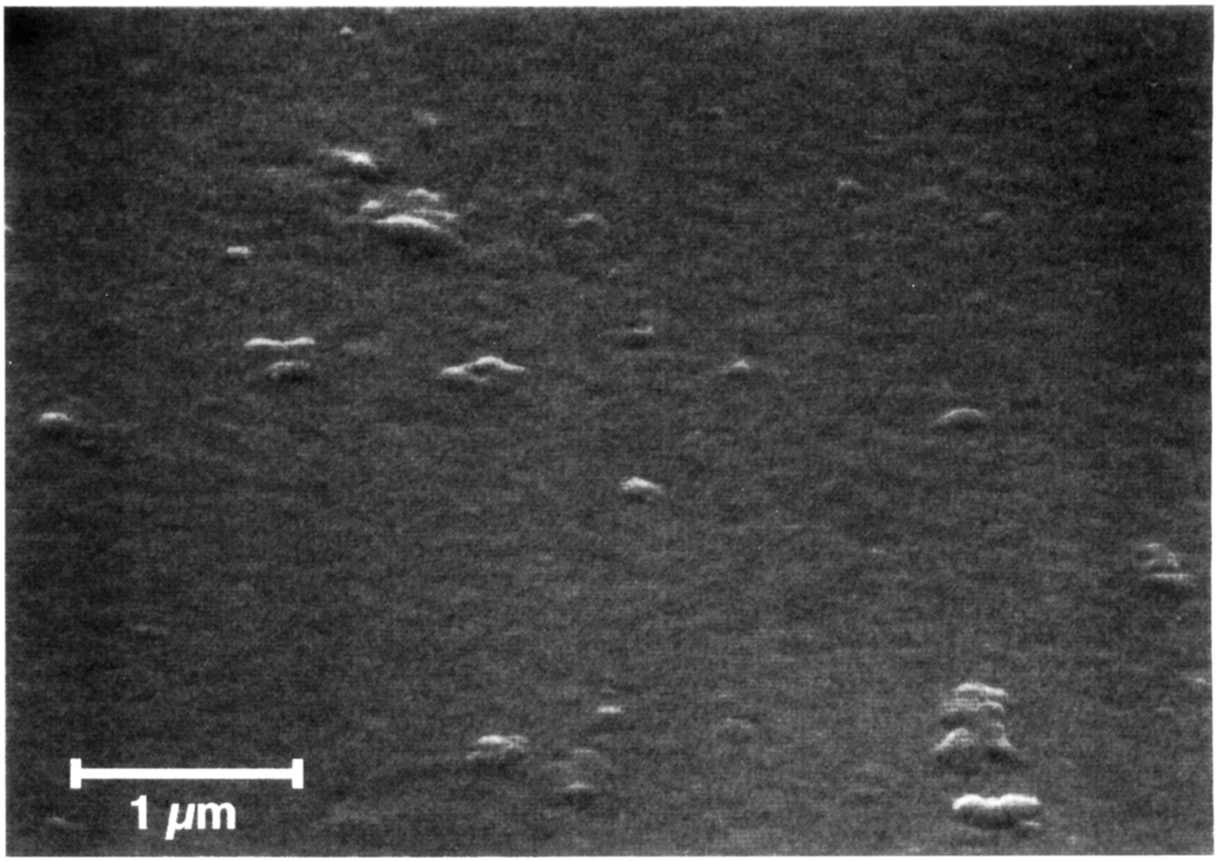

Figure 1. Scanning electron micrograph of $LiNbO_3$ film deposited on (0001) Al_2O_3 at 463 °C.

the ethanol reaction solvent[11,16]) and recrystallized twice from ethanol. The structure of $LiNb(OEt)_6$ has been determined by single-crystal X-ray diffraction and shown to be polymeric with ethoxide bridges linking the metals.[11] Although Mehrotra et al.[16] have reported that $LiNb(OEt)_6$ decomposed to $Nb(OEt)_5$ on attempted sublimation at 0.2 mmHg, we do not believe significant decomposition of the precursor is occurring in our process since the resulting films are of very high quality and have the correct stoichiometry. This is probably due to the short times involved between heating of the precursor and its subsequent deposition on the substrate surface.

Toluene solutions of the precursor (0.01 M) required stirring for ca. 48 h to effect complete dissolution of the double alkoxide. The resulting solutions were added to the spray MOCVD reactor reservoir in a glovebox, and the film fabrication was carried out using the reactor previously described in detail.[14] The slow dissolution of the double alkoxide may be due to a depolymerization process that gives less associated (and more volatile) species. The double alkoxides, $MTi(O\text{-}i\text{-}Pr)_5$ (M = Na, K) have been shown to be infinite chain polymers in the solid state but dissolve in benzene to give dimers.[17]

A typical film deposited on (0001) Al_2O_3 at 463 °C was shown by scanning electron microscopy (SEM) to have a very smooth surface morphology (Figure 1). The presence of occasional surface defects can be noted in the micrograph. These defects are probably caused by particle formation resulting from the gas phase decomposition of the precursor, a relatively common problem for hot-wall reactors operating at atmospheric pressure. Modification of the reactor to accommodate low-pressure delivery of the precursor would be expected to remove these residual defects. The film was identified as monophasic $LiNbO_3$ by its X-ray diffraction pattern (Figure 2). Elemental analysis (ICP), after dissolution of the film in 49% HF, gave atomic percentages of 47.8 ± 0.8 for lithium and 51.0 ± 0.1 for niobium.

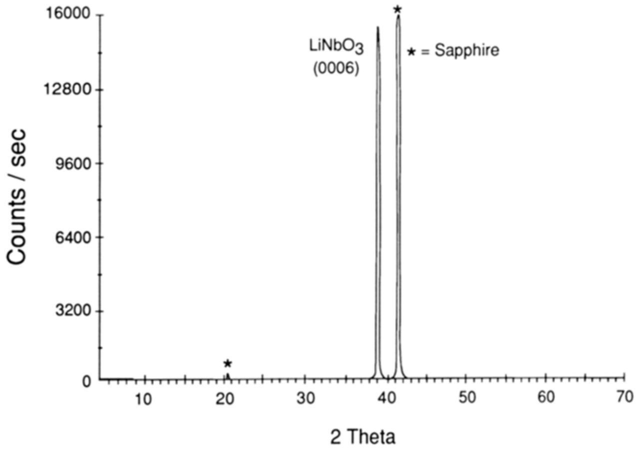

Figure 2. X-ray diffraction pattern of $LiNbO_3$ film deposited on (0001) Al_2O_3 at 463 °C.

The crystalline quality of the film was analyzed by X-ray diffraction and Rutherford backscattering (RBS) analysis. X-ray diffraction identified only a single, highly oriented $LiNbO_3$ phase in the film. Using a Bragg–Brentano parallel optics diffractometer, *c*-axis (planar) alignment of the films was determined by rocking curve analysis.[18] The rocking curve full width half-maximum (fwhm) obtained for the film was 0.38 θ°, which indicates a high

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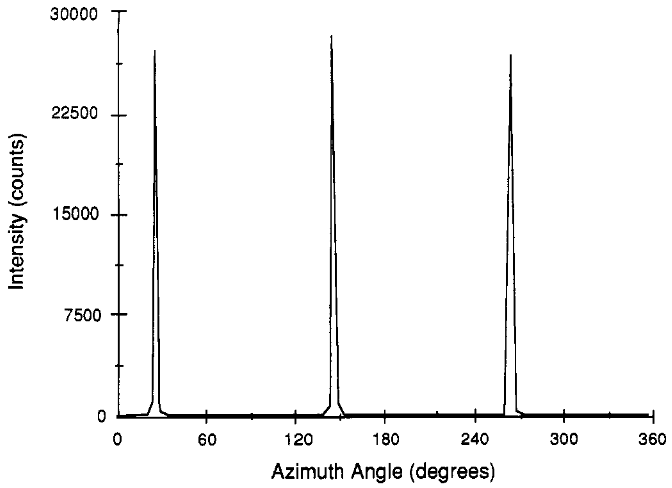

Figure 3. (0112) azimuth plot from the pole figure analysis for the $LiNbO_3$ film deposited on (0001) Al_2O_3 at 463 °C.

degree of alignment along the *c* axis. The corresponding value for a $LiNbO_3$ single crystal was found to be 0.22 θ° when using this geometry. Pole figure analysis was used to determine the in-plane orientation of the film with respect to the sapphire substrate. Using a four-circle goniometer, (0112) pole figures were collected for the $LiNbO_3$ film and the sapphire substrate. Pole figure azimuth data indicated that the $LiNbO_3$ films were in-plane aligned with only about 1% twinning being detectable in the sample (Figure 3). In our previous work,[10] in which $LiNbO_3$ was deposited at 590 °C on the same substrate using a single-source precursor reagent generated in situ from Lidpm and $Nb(OEt)_5$, a rocking curve fwhm of 0.48 θ° was obtained and the pole figure analysis of the film indicated ca. 7% twinning.

Further evidence for the high-crystalline quality of the film was obtained from Rutherford backscattering-channeling measurements that gave a minimum channeling yield of 7% (Figure 4). The corresponding value for single crystal material was measured as ca. 3% while our previous MOCVD process gave films with a value of 20%.[10] The shape of the aligned spectrum indicates that the epitaxial $LiNbO_3$ film has some misorientation as a result of disorder at the interface. This probably results from the 8% lattice mismatch between sapphire and the lithium niobate.[19] Since previous reports describing the fabrication of $LiNbO_3$ films generally do not give such detailed information on film orientation and surface morphology, further comparison with films fabricated by other techniques cannot be made.

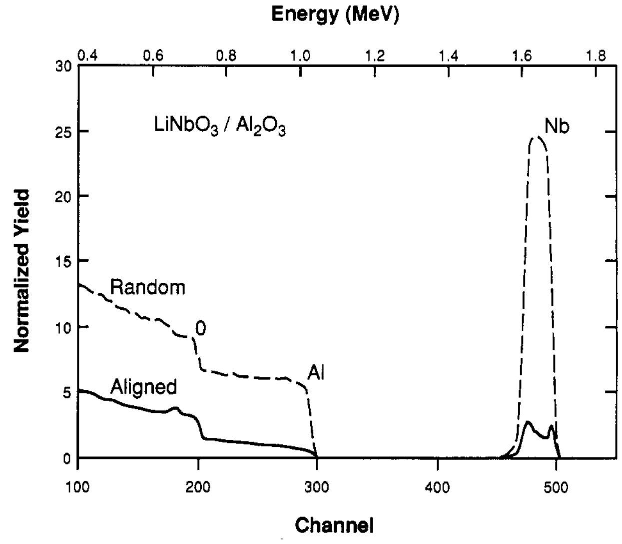

Figure 4. RBS analysis of $LiNbO_3$ film deposited on (0001) Al_2O_3 at 463 °C.

The measurement of the film's index of refraction by prism coupling (Metricon Model 2010 prism coupler), was attempted; however, the film was not thick enough (i.e., <3000 Å) to independently determine the thickness and index of refraction. The preparation of thicker films for optical characterization is in progress.

In summary, we have demonstrated for the first time the MOCVD fabrication of epitaxial films of $LiNbO_3$ using a well-characterized single-source precursor. Because of the low volatility of the solid $LiNb(OEt)_6$, a spray MOCVD process was used to transport the precursor into a hot-wall reactor via a mist of a toluene solution. The $LiNbO_3$ films prepared in this work have been shown to have significantly improved crystalline properties and surface morphology compared to films prepared by previous MOCVD processes.[9,10] We are currently investigating the use of other more volatile monomeric alkoxides for the MOCVD fabrication of $MM'O_3$ (M = Li, K; M' = Nb, Ta) thin films.

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