ANNEXURE
SYNTHESIS OF LITHIUM NIOBATE THIN FILMS.
INTRODUCTION.

Lithium niobate has become a material of significant importance in the context of modern technology because of its unique piezoelectric, electro-optic and nonlinear properties. It is most widely used in surface acoustic wave (SAW) devices, optical waveguides and other photonic devices. Conventionally, such devices are fabricated primarily in single crystal material but use of high quality thin films could offer many advantages in the design of such devices. Recently epitaxial films of the oxide superconductors have been realised on LiNbO$_3$ and this is likely to be transported into the futuristic superconducting-optoelectronics. A variety of methods such as liquid phase growth, growth via melting and r.f. sputtering etc. have been reported for preparing high quality stoichiometric films of LiNbO$_3$ and these have met with some success. Unfortunately, the liquid and melting based methods are not compatible with the modern dry processing approaches. There has been one report on laser ablation from LiNbO$_3$ to examine the dependence of ablation rate on spot size. But, no reports indicate direct evidence of film growth. In this chapter the results of systematic studies on excimer laser ablation of LiNbO$_3$ for film deposition have been reported and it has been shown that stoichiometric films can be obtained by suitable choice and pressure of the ambient.

EXPERIMENTAL.

Lithium niobate pellets sintered at 1000°C for 1 hr were used as target materials to deposit the thin films of LiNbO$_3$ using pulsed excimer laser vaporization technique. The target was mounted in a vacuum chamber capable of rendering a vacuum of better than 10$^{-7}$ Torr. A KrF excimer laser ($\lambda$ = 248 nm) was used as the energy source and the energy density used was 2.3 J/cm$^2$. Laser beam was made incident on the pellet surface at an angle of 45° and the pulse repetition rate was kept at 5 Hz. The target holder was continuously rotated during deposition to avoid undesirable texturing of its surface. The substrate of (100) Si was located at a distance of 5 cm from the target and it was heated to 600°C during deposition. Several cases of depositions in oxygen, argon, vacuum as well as oxygen-argon mixture as ambients were examined. The thickness of the films deposited under different conditions was of the order of few thousand Å. The depositions carried out in vacuum and
in the ambients of oxygen or argon led to mixture of lithium rich and lithium deficient phases alongwith the desired lithium niobate phase. After number of such trials, stoichiometric films could be obtained by means of a new concept of oxygen dilution developed by us, in which a specific mixture of argon and oxygen gases was introduced simultaneously in the chamber. The films were then subsequently characterized by low angle x-ray diffraction, infra red spectroscopy, and spectroscopic ellipsometry.

RESULTS AND DISCUSSION.

The sintered lithium niobate pellet was verified to have single phase character before using it as a target for laser ablation. Low angle x-ray diffraction pattern of LiNbO₃ pellet is shown in Fig.5.1(a) [angle of incidence (a) = 1°]. All the observed peaks match closely with the reported data.¹³ Fig.5.1(b) is an infra-red transmission spectrum of lithium niobate powder (99.99 % pure). It gives absorption bands at 670 cm⁻¹, 580 cm⁻¹, 440 cm⁻¹, 360 cm⁻¹ and 325 cm⁻¹. The pellet prepared from this powder was used as the target material to deposit thin films of LiNbO₃. First the deposition was carried out in oxygen partial pressure of 200 mTorr, energy density 2.3 J/cm² and substrate temperature of 600°C. The x-ray diffraction pattern has shown the presence of LiNb₂O₆ and Li₃NbO₄ phases alongwith LiNbO₃ phase; bringing out the inhomogeneous multiphase character of the film deposited under this condition. Also, deposition was attempted at a higher oxygen partial pressure of 400 mTorr keeping energy density and substrate temperature constant. The x-ray diffraction pattern for the corresponding film gave similar results as in the previous case except for small changes in relative contributions of the phases. In another attempt the oxygen partial pressure was kept constant at 400 mTorr and the other two parameters viz. energy density and substrate temperature were reduced to 1.8 J/cm² and 400°C respectively. This too showed inhomogeneous multiphase character. After annealing these films, no major change was observed in their structural features. This leads to the conclusion that stoichiometric LiNbO₃ films can not be deposited in pure oxygen ambient. It was felt that the reactive character of oxygen in the surface sputtering context may be responsible for this occurrence. Hence, deposition was tried in Ar ambient (400 mTorr, 2.3 J/cm² and 600°C), since Ar can lead only to physical and no chemical sputtering. In another experiment, a deposition was carried out at low background pressure of 5 x 10⁻⁷ Torr (2.3 J/cm² and 600°C). In these cases as well the films showed lithium rich and lithium deficient phases alongwith the desired LiNbO₃ phase. IR transmission results for the films deposited in oxygen (400 mTorr, 2.3 J/cm² and 600°C), argon
1. Low angle x-ray diffraction patterns for films laser deposited at an energy density of 2.3 J/cm², T$_{sub}$ of 600°C and in a gas mixture of (a) 300 mTorr Ar and 200 mTorr O$_2$; (b) 400 mTorr Ar and 100 mTorr O$_2$ and (c) 450 mTorr Ar and 50 mTorr O$_2$.

Fig. 1. Low angle x-ray diffraction patterns for films laser deposited at an energy density of 2.3 J/cm², T$_{sub}$ of 600°C and in a gas mixture of (a) 300 mTorr Ar and 200 mTorr O$_2$; (b) 400 mTorr Ar and 100 mTorr O$_2$ and (c) 450 mTorr Ar and 50 mTorr O$_2$. 

- LiNbO$_3$
- LiNb$_3$O$_8$
- Li$_3$NbO$_4$
ambients and in vacuum also indicated that the nature of the transmission pattern under none of these cases matched with that for the bulk stoichiometric LiNbO$_3$ sample. Thus, a different approach to the selection of the nature of the ambient and its partial pressure was considered necessary.

Earlier work reported on sputter deposition of LiNbO$_3$ films$^{10,14}$ has brought out that high quality stoichiometric films of this material can be obtained only by using an appropriate gas composition comprising of argon and oxygen. Laser deposition also leads to surface partial bombardment effects somewhat similar to the case of sputter deposition. Hence it was considered interesting and useful to deposit films by laser ablation in argon and oxygen gas mixtures at different partial pressure ratios. This indeed has been the first attempt at laser deposition in mixed gas ambient.

First a mixture of 300 mTorr Ar and 200 mTorr O$_2$ was used during deposition. Interestingly, the major component of the phase observed in the film is LiNbO$_3$, though a small amount of LiNb$_2$O$_5$ phase is also seen to be present [Fig. 1(a)]. Upon increasing the relative Ar partial pressure [400 mTorr Ar and 100 mTorr O$_2$] the LiNb$_2$O$_5$ could be significantly reduced and a stoichiometric LiNbO$_3$ film could be obtained as seen from the XRD pattern of this film shown in Fig. 1(b). The x-ray data for the two cases of 300 mTorr Ar/200 mTorr O$_2$ and 400 mTorr Ar/100 O$_2$ are similar, but the IR signatures differ significantly, as will be brought out. It is important to mention however that a further increase in the relative Ar partial pressure [450 mTorr Ar and 50 mTorr O$_2$] was found to lead to a mixture of different phases. [Fig. 1(c)]. The IR transmission data for the above three cases of interest are given in Fig. 2. Eventhough all the common IR signatures are seen in the films deposited under the said three conditions, the resemblance of the entire spectrum to that for the bulk stoichiometric material is seen only in the case of the film deposited at 400 mTorr Ar and 100 mTorr O$_2$. The high quality character of the film deposited under this condition was also verified by spectroscopic ellipsometry measurements. The result given in Fig. 3 shows the value of refractive index to be in the range between 2.2 - 2.4 over the entire spectral range, which indeed is the known response for a high quality stoichiometric material$^{15}$.

Few comments may now be made on these observations. A given ambient controls the physical properties as well as the chemical constitution of the laser generated plasma. These features are transported to the growing film surface via intermediate relaxations and decide the composition of neutral/ionised radicals impinging on the surface as well as velocity (energy) distributions. These factors together control the surface chemistry/compound formation and the sputter removal
Fig. 2. IR transmission data for films laser deposited at an energy density of 2.3 J/cm$^2$, T$_{\text{sub}}$ of 600°C and in a gas mixture of (a) 300 mTorr Ar and 200 mTorr O$_2$; (b) 400 mTorr Ar and 100 mTorr O$_2$, and (c) 450 mTorr Ar and 50 mTorr O$_2$. 
Fig. 3. Spectroscopic ellipsometric data for LiNbO₃ film deposited at an energy density of 2.3 J/cm², Tsub of 600°C and in a gas mixture of 400 mTorr Ar and 100 mTorr O₂.
phenomena. Depending on the nature of the material system and the properties of its subcomponents, a window of parameter space may appear which can lead to autocompensation various factors, leading to achievement of the desired stoichiometry. However, given the complexity of the participating processes, this can not be guaranteed for almost any system unless the process offers flexible deposition parameters. Use of a gas mixture is, in our view, a way of achieving this. For instance if the case of 100 mTorr oxygen Vs a mixture of 100 mTorr oxygen with 400 mTorr argon are compared, the plasma expansion properties and the velocity distributions of radicals impinging on the growing surface are expected to be significantly different; though the quantity of reactive oxygen is comparable. Argon, in fact, can provide the adequate scattering environment for dissipation of the kinetic energy of the radicals without directly affecting the gross composition of those components in the plasma which have a chemical influence on the process. Thus the choice of a mixed ambient and the relative partial pressures of the component gases offer further flexibility in stoichiometry control via control of the ablation deposition process itself.

CONCLUSION.

Stoichiometric thin films of lithium niobate have been successfully deposited on (100) Si by pulsed excimer laser ablation in a mixture of 400 mTorr argon and 100 mTorr oxygen. It is shown that the choice of the ambient is critical to the attainment of stoichiometry in the case of this material. The idea of using mixed ambients during laser ablation-deposition, employed for the first time in this work, is demonstrated to offer distinct advantage in the context of control of film properties. The other two parameters viz laser energy density and substrate temperature used were 2.3 J/cm² and 600°C respectively.
REFERENCES