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Electrochemical lithium insertion in sol-gel deposited $LiNbO_3$ films

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Abstract

Inorganic $LiNbO_3$ ion conducting films were prepared by sol-gel process involving two alkoxides, lithium ethoxide and niobium ethoxide. The films were analyzed by ellipsometry, X-ray diffractometry, scanning electron microscopy and impedance spectroscopy. Impedance spectroscopy indicated that the Li^+ conductivity values were in the range of $6–8 \times 10^{-7}$ S cm^{-1}. The morphology and thickness of these films played an important role in the insertion of lithium ions. Spectrophotometric investigation showed that $LiNbO_3$ films exhibit very weak cathodic coloration from 350 to 900 nm spectral region. The electrochemical and optical properties clearly indicate that sol-gel deposited $LiNbO_3$ films can be used as lithium ion conducting layers for electrochromic device application.

1. Introduction

In recent years, there has been considerable interest in inorganic ion conductors for use in solid-state batteries, electronic displays or memory devices [1]. In the early 1980s', the development of electrochromic (EC) materials to the fabrication of "smart windows" has prompted increased interest in ion conductor studies, especially those aimed at finding new transparent ion conductors. Unfortunately, although a large number of studies can be found on inorganic ion conductors spanning the last 20 years, only a few metal oxides such as Ta_2O_5, Nb_2O_5 Cr_2,O_3, ZrO_2 and SiO_2 are known to be suitable for EC devices [2–7]. But even these materials have specific drawbacks or are limited to use in only proton devices.

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Lithium niobate is a ferroelectric film which has been used in several electrooptical applications, such as, optical modulators, surface acoustic wave devices [8,9]. Fabrication of high optical quality $LiNbO_3$ films for non-EC applications can be obtained by rf sputtering [10] molecular beam epitaxy [11], laser ablation [12] and sol-gel deposition [13,14]. Seward et al. reported [15] that RF-sputtered glassy $LiNbO_3$ films exhibit an ionic conductivity of about 10^{-7} S cm^{-1} and could be used in electrochromic (EC) devices.

In this study, we report on $LiNbO_3$ films produced by the sol-gel process for ion conductors in electrochromic devices (Fig. 1). Several aspects of these coatings are covered, beginning with sol-gel deposition of $LiNbO_3$ films on fused silica, glass and indium tin oxide (ITO) coated glass. The structural, chemical and electrochemical properties of these films are detailed. We also report on the optical properties and ionic conductivity of $LiNbO_3$ films.

The major advantages of the sol-gel process are low-cost, with good control of film stoichiometry and porosity. Also, from a commercial view point, a much lower capital investment in equipment is needed to produce the films compared to vacuum deposition processes. These factors are especially important in the fabrication of $LiNbO_3$ films as transparent lithium ion conducting materials for electrochromics.

2. Experimental

Lithium ethoxide (99.9%) and niobium pentaethoxide (99.99%) (Aldrich Chemicals, Green Bay, WI) were used for synthesis. The polymeric solutions were prepared from lithium ethoxide and niobium pentaethoxide in an ethanolic environment. The preparation of a mixed metal alkoxide precursor solution is briefly illustrated in Fig. 1. A 0.5 M stock solution was prepared by mixing alkoxide and a small amount of water, (0.5%). This solution was stirred into ethanol. The stirring of the solution was continued for 10 min. The solution was then further diluted with ethanol and stirred for 2 hours forming a polymeric solution. The resulting polymeric solution was used as the deposition material. The polymeric solutions were very stable for several weeks. This is very significant for sol-gel processing, as many coating solutions have short lifetimes.

Films were deposited onto fused silica, glass and ITO coated glass (Donnelly Corp., Holland, MI) by spin coating technique; however, a dip coating technique could be used too. The substrates was spun with a speed of 1500 rpm for 40 s. The deposition conditions were optimized to obtain the most homogeneous films with the best thickness. Normally, six to seven depositions are required to obtain a film of 250 nm film. After each deposition, the film was dried at 150°C for 10 min. and then spin-coated successively. The films were finally heat-treated at 450°C and 550°C for 60 min. at the heating and cooling rate of 2°C/min.

Various techniques were employed to characterize the morphology, microstructure and electrooptical properties of the $LiNbO_3$ films. Structural investigation was performed by a Siemens Krostalloflex X-ray diffractometer (XRD) with Ni filtered

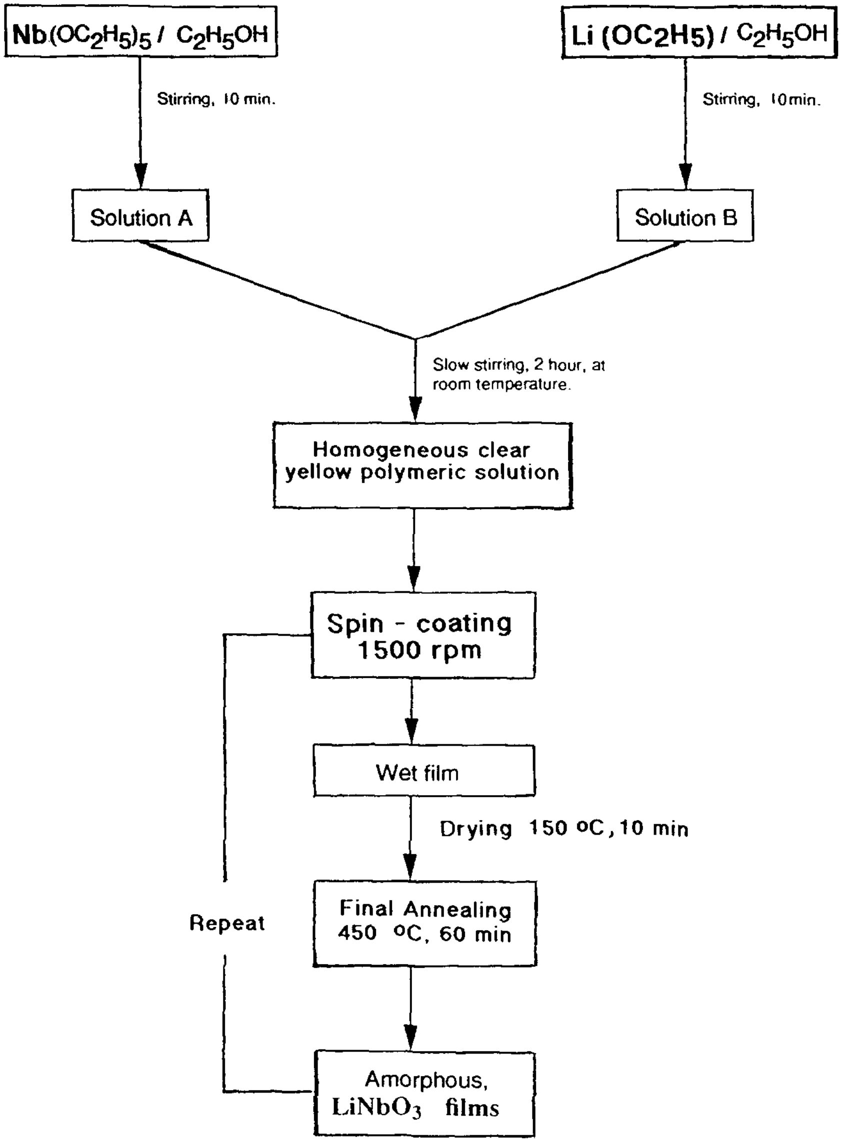

Fig. 1. Process flow chart for sol-gel $LiNbO_3$ film preparation.

CuK_α excitation. The surface morphology of the films examined using a JEOL JSM-6400 scanning electron microscope (SEM) with accelerating voltage of 20 KV. The thickness of the films were measured by a Dektak II (Veeco Inst. Inc.) surface profiler. The refractive indices values were determined by an Sopra, Model SE 4G spectroscopic ellipsometer over the 300–800 nm wavelength range. The optical transmittance of the films were measured in the wavelength range of 250 to 900 nm on a Perkin-Elmer Lambda UV/VIS-NIR spectrophotometer. The ionic conductivities of the lithium niobate films were measured by an AC complex impedance technique. The equipment used was a Schlumberger, SI1260, Impedance/Gain analyzer, driven by a PAR model 273 potentiostat/galvanostat and electrochemical interface that were programmed by a desktop computer for data collection and analysis. Cyclic voltammetric measurements were done using a digital coulometer (PAR) and a Hewlett-Packard X–Y chart recorder. The electrochemical cell consisted of a three electrode configuration in a sealed cell. The working electrode was $LiNbO_3$ on ITO glass, with a lithium or Ag/AgCl counter-electrode and lithium or platinum reference electrode. The electrolyte was anhydrous 1M $LiClO_4$ in propylene carbonate (PC) prepared in a dry box.

3. Results and discussion

Optimal conditions to obtain high quality films of $LiNbO_3$ were established by changing many parameters such as types of alkoxide ligand, concentration of the solvent and stirring time. The preparation of the high quality films, is largely dependent on viscosity of polymeric solution which was controlled by the amount of water added. Homogeneously grown Li^+ ion conducting films were fabricated using six coating cycles. The thickness profile measurement of the heat treated (450°C) $LiNbO_3$ films indicate that the average thickness of a single coating is 53 nm. The thickness of a film with six coatings is about 250 nm. Fig. 2a and 2b show the XRD patterns for films grown on the glass substrate which were annealed at 400°C and 550°C for 60 min., respectively. As shown in Fig. 2a the films were

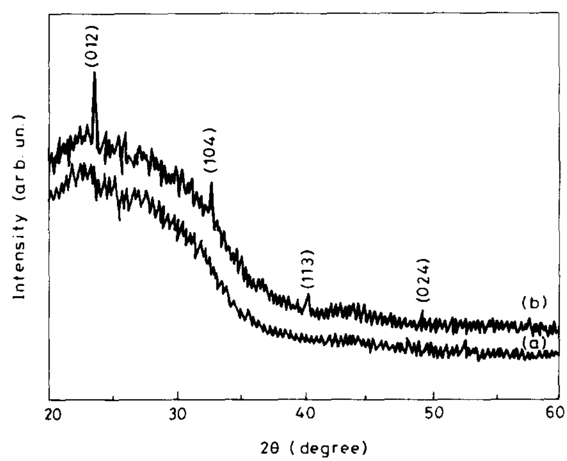

Fig. 2. XRD patterns of $LiNbO_3$ films on a glass substrate heat-treated at (a) 450°C for 60 min., showing an amorphous structure (lower plot) and (b) 550°C for 60 min., showing the trigonal $LiNbO_3$ structure (upper plot)

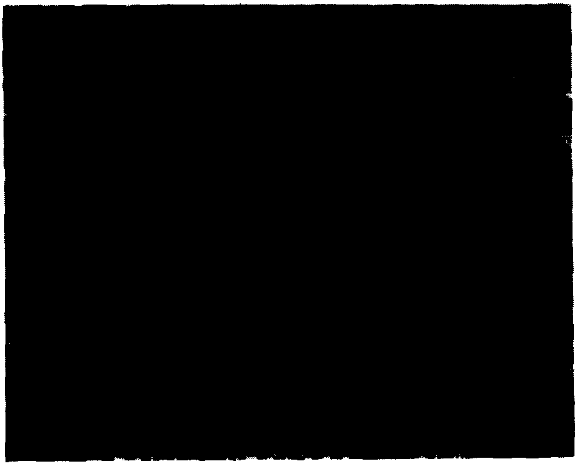

Fig. 3. SEM micrograph of the surface of amorphous 400°C heat treated $LiNbO_3$ film deposited on glass. The crystalline films are similar in microstructure.

prepared from $Li(OC_2H_5)$ and $Nb(OC_2H_5)_5$ precursors were amorphous. Moreover, they remained amorphous after heat treatment for 5 hours at 500°C, crystallization occurred at 550°C (Fig. 1b). The crystallized coating corresponds to the trigonal structure of $LiNbO_3$.

A SEM micrograph of a typical surface microstructure of amorphous $LiNbO_3$ film on glass is shown in Fig. 3. The morphology of the films exhibited a smooth and adherent surface with very few pinholes or microcracks over a large area. The morphology of the film on the ITO substrate is more porous and inhomogeneous than that of the films coated on glass substrates. When the film was heat treated at 550°C, the surface morphology was changed to be homogeneous. Upon crystallization very little change is seen in the micrograph.

Optical properties of $LiNbO_3$ films were studied to determine deposition densification conditions appropriate for good optical quality coatings. The spectral dependence of the refractive index value of films on fused silica substrate are shown in Fig. 4. The refractive index, n, varied continuously from 1.91 to 1.97 $\pm$ 0.01, with k values below 10^{-4} over the 300–800 nm range. As heat treatment temperature increased, films became more transparent and the refractive index value increased slightly. These data are consistent with the SEM micrographs in which the films have a smooth and dense surface.

In order to investigate the electrochemical properties of the films, cyclic voltammetry was performed at room temperature on ITO coated glass in an electrolyte of 1 M $LiClO_4$ in propylene carbonate (PC). Fig. 5 shows the cyclic voltammogram of films heat treated at 450°C for 60 min. Cyclic curves at the fifth cycling are show in this figure as a steady cycling behavior was observed after 3–4 cycles. We have measured the charge on the cathodic and anodic sides of this voltommogram and found it to be roughly equal. The currents however are

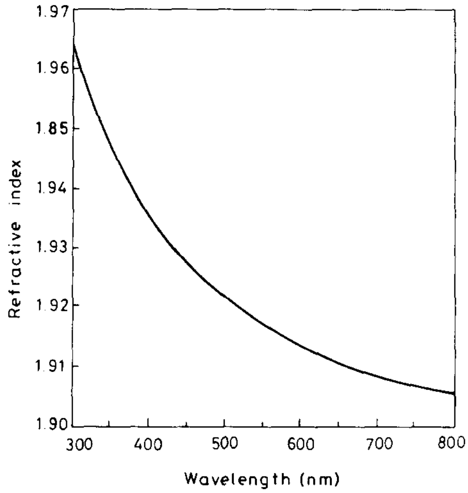

Fig. 4. Spectral dependence of the refractive index, n of amorphous sol-gel deposited $LiNbO_3$ film on fused silica (400°C) (the curve was plotted from 100 data points).

different by a factor of two due to large impedance changes in the electrode between intercalation/deintercalation of Li^+. It appear to us that Li^+ is the only reasonable intercalation species. An increase in the cathodic current was observed

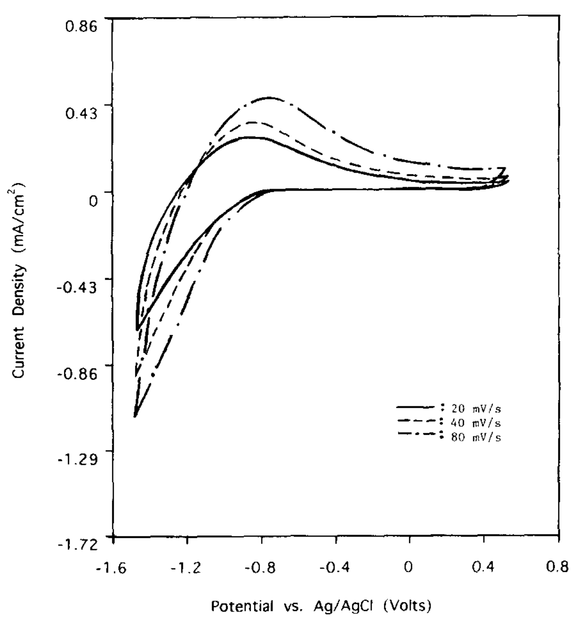

Fig. 5. Cyclic voltammograms for Li^+ intercalation/deintercalation in amorphous $LiNbO_3$/ITO/glass electrodes in 1 M $LiClO_4$/PC. Different scan rates are shown.

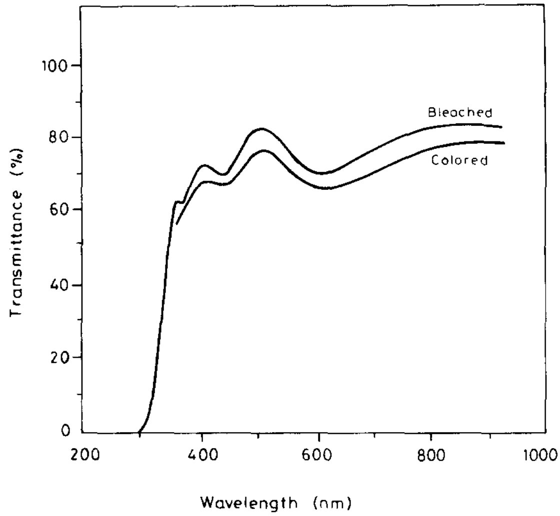

Fig. 6. In-situ visible transmittance measurements of a $LiNbO_3$/ITO/glass electrode in 1 M $LiClO_4$/PC electrolyte. Shown are the bleached and colored conditions ($V = 1.2$ V versus Li).

at a potential of 0.8 to 1.5 V versus Ag/AgCl. In the positive voltage sweep an anodic current peak appeared at 0.8 V. Application of a cathodic potential against Ag/AgCl electrode resulted in electrochemical lithium insertion to the $LiNbO_3$ layer. Successive cycles are superimposed over one another and almost a single curve is observed during intercalation/deintercalation for over 1200 cycles suggesting that the electrochemical insertion is reversible and the redox reaction is stable. The spectral optical properties were studied by in-situ switching in the spectrophotometer. The in-situ cell consisted of 1 M $LiClO_4$/PC electrolyte with a $LiNbO_3$/ITO/glass working electrode and lithium reference and counter electrodes. The transmittance data is shown in Fig. 6, for bleached and colored conditions (1.2 V versus Li).

The integrated photopic transmittance varied from 75% to 70% between bleached and colored. For an ion conductor high transmission with low coloration is desired.

In order to investigate the ionic conductivities of $LiNbO_3$ films, measurements of complex impedance were made over the frequency range of 100 mHz to 60 KHz. The impedance data was plotted on the complex plane. A simplified equivalent circuit representing the sample was used to calculate ionic conductivity (shown in the inset in Fig. 7) where R_e is the resistance of electrodes, C_d is the double layer capacitance, R_i is the ionic resistance, and C_g is the geometric capacitance between electrodes. Fig. 7 shows a typical AC impedance spectra of a $LiNbO_3$ film. The electrolyte and the electrode–electrolyte interface effect are evident by the presence of the semicircle at higher frequencies and an inclined spike at lower frequencies. The lithium conductivity was determined from the bulk resistance (the

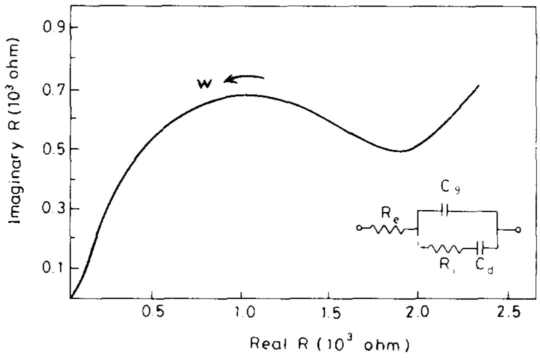

Fig. 7. Typical impedance plot of a crystalline $LiNbO_3$ film (240 nm thick). Ionic conductivity is $\sigma = 8.4 \times 10^{-7}$ S cm^{-1}. The inset shows the equivalent circuit used for analysis.

diameter of the semicircle) and the geometrical factors (the thickness and the electrode area) [16]. The values of ionic conductivities varied from 6.1×10^{-7} to 8.4×10^{-7} S cm^{-1} depending on the heat treatment temperature. Higher heat treatment temperatures produced denser films, decreasing conductivity. Denser films in turn provide less surface area. The ionic conductivity decreases according to the increase of packing density by annealing at high temperatures. The electronic resistivity of $\rho = 19.2$ ohm-cm.

The stoichiometry of each film was thought to be roughly equal because the refractive index were estimated to be almost the same from an ellipsometric measurement.

4. Conclusions

Amorphous and crystalline lithium conducting $LiNbO_3$ films were fabricated on fused silica, glass and ITO coated glass substrates by the sol-gel method using lithium and niobium ethoxide as precursor materials. These films were transparent and very strong mechanically. The best uniformity was observed at a spinning rate of 1500 rpm. The refractive index, n, ranged from 1.91–1.97, with a very low k value, over the visible region. The amorphous $LiNbO_3$ films had ion conductivities of 8.4×10^{-7} S cm^{-1}, while the electronic resistivity was quite high, 19.2 ohm-cm. Although the ionic conductivity of sol-gel deposited electrolyte $LiNbO_3$ film is lower than that of polymeric ion conductors (10^{-5} to 10^{-6} S cm^{-1}), this inorganic material has the advantages of stability at higher temperatures and good mechanical strength. Currently, device application studies with use of amorphous sol-gel deposited $LiNbO_3$ films are being undertaken to integrate these layers into electrochromic devices in the future.

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