

# Study of crystallization of LiNbO<sub>3</sub> films from metal alkoxides

S. HIRANO, T. YOGO, K. KIKUTA, Y. ISOBE

*Department of Applied Chemistry, Nagoya university, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan*

S. ONO

*\* Nagoya Municipal Industrial Research Institute, Rokuban, Atsuta-ku, Nagoya 456, Japan*

The crystallization process of epitaxial LiNbO<sub>3</sub> films on sapphire (0001) substrates was investigated by Raman microprobe spectroscopy. LiNbO<sub>3</sub> gel films were prepared by the sol-gel method using metal alkoxide precursors on sapphire (0001) substrates and heat treated at various temperatures below 500 °C to produce epitaxial LiNbO<sub>3</sub> films. Analyses by electron spectroscopy for chemical analysis and SEM revealed LiNbO<sub>3</sub> films were stoichiometric and homogeneous. Raman spectra of the film prepared at 250 °C indicated that the NbO<sub>6</sub> octahedral coordination structure in LiNbO<sub>3</sub> began to form as the initial state of crystallization. As the heat-treatment temperature was raised, the Raman bands became sharper and increased in spectral intensity and were seen to be the characteristic Raman bands of crystalline LiNbO<sub>3</sub>. Refractive indices of the obtained films indicated appropriate values. As a method to crystallize the more highly preferred orientation to (006) LiNbO<sub>3</sub> film at relatively low temperature, the formation of an underlayer film from diluted solution prior to multiple dip-coating, was found to be very promising.

## 1. Introduction

LiNbO<sub>3</sub> is an important ferroelectric material due to its excellent pyroelectrical, piezoelectrical, electro-optical and photorefractive properties. It has useful applications for surface acoustic wave devices, waveguides in integrated optics, infrared sensors, etc. Single crystals have routinely been grown from melts with the congruent composition, which is 48.45 mol % Li<sub>2</sub>O, by means of the Czochralski method. However, the Li<sub>2</sub>O deficiency from stoichiometry causes compositional defects, and thus disadvantages for physical properties, especially the optical property of LiNbO<sub>3</sub>. The synthesis of stoichiometric crystalline LiNbO<sub>3</sub> has been studied to evaluate the effect of defects on the physical properties. In addition, ferroelectric thin films are required to satisfy the demands for miniaturizing and integrating the devices.

We have already reported studies on preparations of stoichiometric crystalline LiNbO<sub>3</sub> powders, epitaxial films and fibres using sol-gel processing with metal alkoxides, through the controlled chemical reaction in solvents under a controlled atmosphere during crystallization [1-6]. The present paper presents the results of a study of the crystallization process by Raman microprobe spectroscopy of LiNbO<sub>3</sub> gel films prepared on sapphire substrates at low temperatures below 500 °C.

## 2. Experimental procedure

### 2.1. Preparation of the LiNbO<sub>3</sub> films

Stoichiometric LiNbO<sub>3</sub> crystalline films with pre-

ferred orientation were prepared as follows. Lithium ethoxide and niobium ethoxide were dissolved in absolute ethanol, subsequently stirred and refluxed at 78.5 °C for 24 h to form the double alkoxide, Li(Nb(OEt)<sub>6</sub>) solution [1]. This was partially hydrolysed with an equivalent mole of water free of CO<sub>2</sub>. After additional refluxing for 24 h, the precursor solution was concentrated to 0.4 mol l<sup>-1</sup>, yielding a homogeneous solution. After fabricating the gel films using the precursor solution by dip-coating on sapphire (0001) substrates, they were heat treated at various temperatures from 250-500 °C in a flow of a controlled water vapour/oxygen mixture for crystallization. Films about 0.3 μm thick were obtained in ten cycles of the dip-coating followed by the heat-treatment procedure.

### 2.2. Evaluation

The orientation and crystallization of prepared LiNbO<sub>3</sub> films were examined by X-ray diffraction (XRD). The distribution of the compositional elements was determined by electron spectroscopy for chemical analysis (ESCA). Film morphology was observed by scanning electron microscopy (SEM).

The crystallization process was studied by Raman microprobe spectroscopy using 488.0 nm line of the Ar<sup>+</sup> laser with 500 mW power. The laser beam was focused on the sample from the perpendicular direction to the *c*-axis (in the *c*-plane) of the oriented LiNbO<sub>3</sub> film. The refractive indices were determined by ellipsometry using a He-Ne 632.8 nm laser beam.

### 3. Results and discussion

#### 3.1. Orientation and crystallization of LiNbO<sub>3</sub> films

Fig. 1 shows the XRD profiles of LiNbO<sub>3</sub> films on sapphire (0001) substrates heat treated under various temperature conditions. Films heat treated at 400 and 500 °C showed highly preferred orientation along the (006) plane. On powders, the (006) diffraction is the line weakest in intensity, which becomes most pronounced following crystallization on sapphire substrates. However, no such preferential orientation was observed in diffraction pattern of the film heat treated at 250 °C.

#### 3.2. Chemical composition

Figs 2 and 3 show the changes in ESCA spectra of the compositional elements (O, C, Nb, Al, Li) for the LiNbO<sub>3</sub> films on sapphire (0001) substrates heat treated at 250 and 500 °C, with Ar<sup>+</sup> sputtering from the film surface to the substrate. The strong intensity of C(1s) appeared at a sputtering time 0:0 (min:s) is due to surface contamination during handling. The reduction of niobium by Ar<sup>+</sup> sputtering induced the whole ESCA spectra to shift towards the lower binding energy regions, causing the lithium photoelectron binding energy region to be covered by the Nb(4s) peak, making the Li(1s) peak indistinguishable. For an Ar<sup>+</sup> sputtering time from 0:3–1:0 (min:s), prominent differences were observed on C(1s) ESCA spectra be-

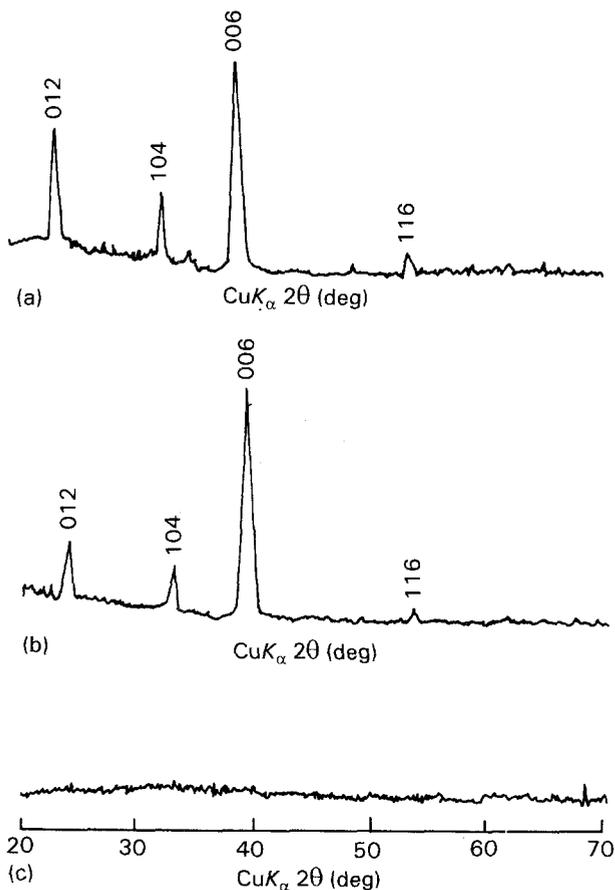


Figure 1 XRD profiles of LiNbO<sub>3</sub> films prepared by the heat treatment at various temperatures. (a) 500 °C, (b) 400 °C, (c) 250 °C.

tween the films heat treated at 250 °C and at other temperatures (400 and 500 °C). In the C(1s) spectra of the film heat treated at 250 °C, an extra peak was observed at 293 eV in the higher binding energy region different from the peak due to carbon contaminants. This peak was not observed on films prepared at other temperatures.

According to the chemical shift principle for ESCA, it is known that when the chemical bonding state of the atom changes, the binding energy changes, because of the electron density alterations by the interaction with surrounding binding atoms. Furthermore, when the atom bonds to other more electronegative ones, the peak position moves to the higher binding energy region. From this standpoint, it is considered that carbon appearing at 293 eV bonds to oxygen in the double bonding state, such as in carbonyl groups. It is assumed that this peak indicates reaction residues derived from ethoxy groups of double alkoxides on heat treatment. After 1:0 (min:s) Ar<sup>+</sup> sputtering time, no remarkable differences nor irregularities in the interfaces between LiNbO<sub>3</sub> films and sapphire substrates were observed in the ESCA spectra of films obtained at various temperatures. Fig. 4 shows the depth profile corresponding to the ESCA spectra of the film obtained at 500 °C (see Fig. 3). In the relative composition of the elements, the distributions of both niobium and oxygen were kept almost constant in ratio with the depth. In addition, this depth profile of relative composition was comparable to that of single-crystal LiNbO<sub>3</sub>. The chemical composition, therefore, was confirmed to be stoichiometric and homogeneous in the LiNbO<sub>3</sub> film.

#### 3.3. Morphology

Fig. 5 shows an edge-on scanning electron micrograph of the film crystallized at 500 °C on a sapphire (0001) substrate. The film appeared to be homogeneous and smooth without any cracks or voids. On the other hand, the surface of the film crystallized at 250 °C revealed some pores and a microstructurally coarser texture than that of the film crystallized at 500 °C. The thickness of the films heat treated at 250 and 500 °C were 0.36 and 0.24 μm, respectively. It is supposed that the increase in thickness of the film heat treated at 250 °C reflects the lower sintering density with pores, which gives rise to a lower refractive index.

#### 3.4. Raman spectral analysis

The crystalline LiNbO<sub>3</sub> is composed of a hexagonal close-packed structure in which the regular NbO<sub>6</sub> octahedra are connected by shared corners with 30° tilting angle between two adjacent NbO<sub>6</sub> octahedra. Its crystal structure has the trigonal symmetry and belongs to the space group R3c. Raman scattering by LiNbO<sub>3</sub> has been studied for over 25 years. The assignments of fundamental optical mode frequencies of LiNbO<sub>3</sub> based upon the Raman spectra are summarized in Table I [7–13].

The Raman microprobe spectra of LiNbO<sub>3</sub> films heat treated at various temperatures are shown in Fig.

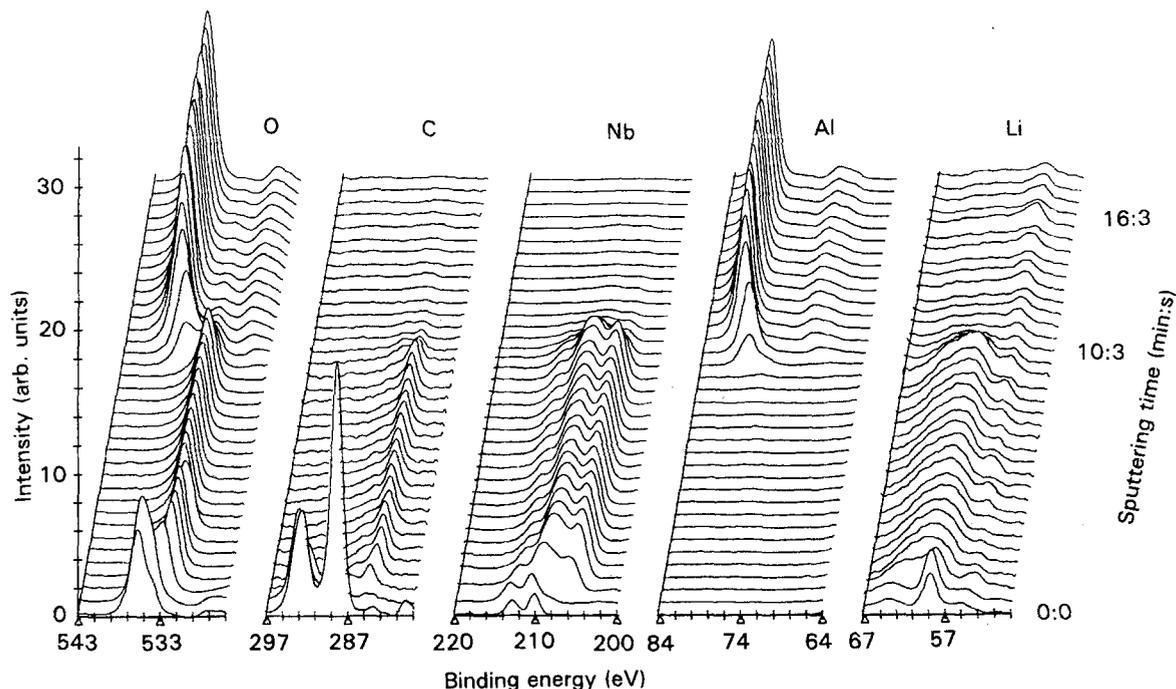


Figure 2 Changes in ESCA spectra in the  $\text{LiNbO}_3$  film heat treated at  $250^\circ\text{C}$  on a sapphire (0001) substrate.

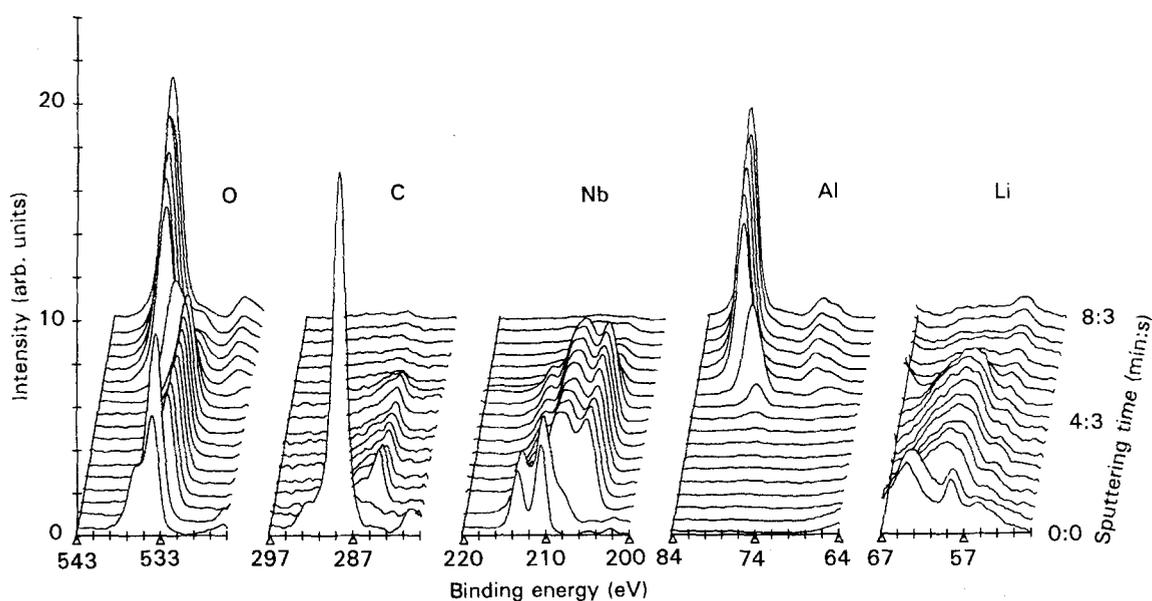


Figure 3 Changes in ESCA spectra in the  $\text{LiNbO}_3$  film crystallized at  $500^\circ\text{C}$  on a sapphire (0001) substrate.

6. The observed spectrum of the film at  $250^\circ\text{C}$  showed weak and broad Raman bands corresponding to the frequency regions of  $\text{LiNbO}_3$  represented in Table I and to be clearly different from those of amorphous gel powders of  $\text{LiNbO}_3$  dried at  $150^\circ\text{C}$ . Major characteristic Raman bands are ascribed to the octahedral  $\text{NbO}_6$  structure in  $\text{LiNbO}_3$  and appear in the  $620\text{--}630\text{ cm}^{-1}$  region with a shoulder at  $580\text{ cm}^{-1}$ . The spectrum indicates that the regular octahedral  $\text{NbO}_6$  coordination in the  $\text{LiNbO}_3$  crystal occurs at  $250^\circ\text{C}$ . In the Raman spectrum of the film at  $400^\circ\text{C}$ , the weak and broad bands at  $580\text{--}630\text{ cm}^{-1}$  and extra bands corresponding to  $A_1$  and  $E$  symmetry modes became sharper and increased in spectral intensity. Finally, the Raman spectrum of the film at  $500^\circ\text{C}$

showed characteristic Raman bands almost exactly corresponding to  $A_1$  and  $E$  symmetry modes of single-crystal  $\text{LiNbO}_3$ . Through the crystallization process, another phenomenon was also observed: major Raman bands corresponding to  $A_1$  and  $E$  symmetry modes gradually shifted to higher frequency regions as the heat-treatment temperature was raised. Although the film at  $250^\circ\text{C}$  does not exhibit a crystalline character in XRD (Fig. 1), the results from Raman spectroscopy suggested that the conformation to the octahedral structure in  $\text{LiNbO}_3$  was initiated during the initial state of crystallization at  $250^\circ\text{C}$ , but was unable to be detected clearly by XRD, and constructed the completed structure through accelerated crystallization at higher temperatures [5].

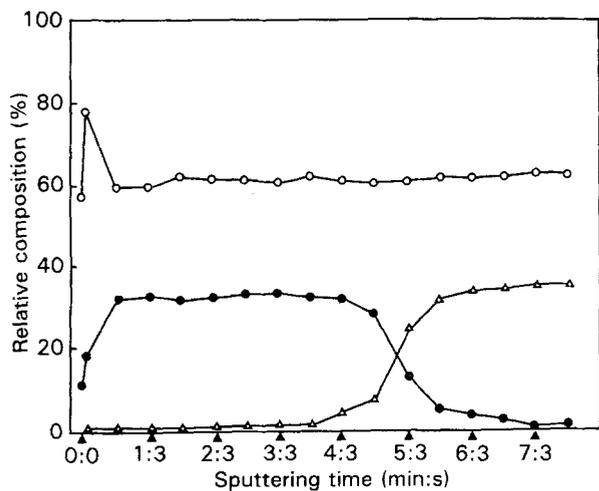


Figure 4 ESCA depth profile of the  $\text{LiNbO}_3$  film crystallised at  $500^\circ\text{C}$  on a sapphire (0001) substrate. (○) O, (●) Nb, (△) Al.

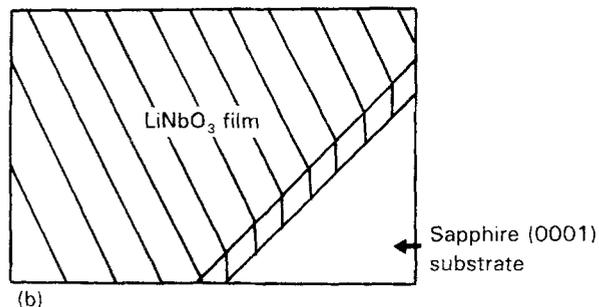
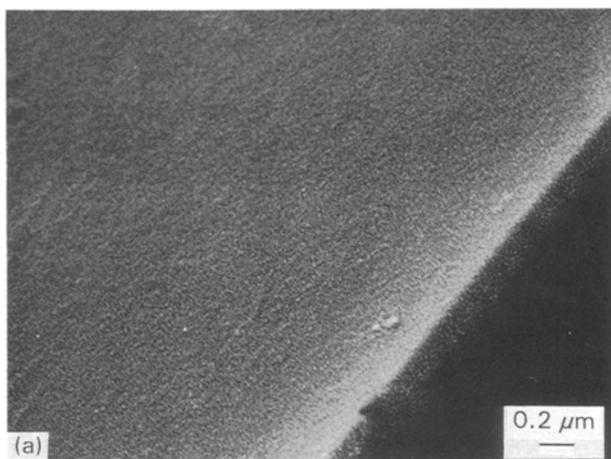


Figure 5 Scanning electron micrograph of the edge-on profile of the fracture surface of the film crystallized at  $500^\circ\text{C}$  on a sapphire (0001) substrate.

TABLE I Symmetries and Raman frequencies ( $\text{cm}^{-1}$ ) of fundamental optical modes in  $\text{LiNbO}_3$

$A_1$	Transverse	252–255, 276, 333, 631–634
	Longitudinal	873
E	Transverse	152, 237–239, 264–266, 321, 367–369, 430–434, 580
	Longitudinal	299, 880–883

### 3.5. Optical property

The refractive indices of  $\text{LiNbO}_3$  films on sapphire (0001) substrates prepared at temperatures from  $250$ – $500^\circ\text{C}$  are summarized in Table II. The measured

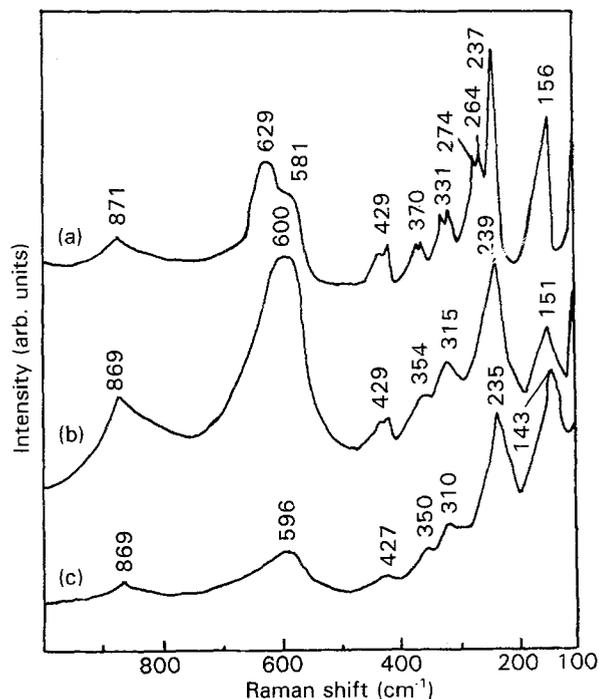


Figure 6 Raman microprobe spectra of  $\text{LiNbO}_3$  films prepared by heat treatment at various temperatures on sapphire (0001) substrates. (a)  $500^\circ\text{C}$ , (b)  $400^\circ\text{C}$ , (c)  $250^\circ\text{C}$ .

values are seen to be in good agreement compared with those of  $\text{LiNbO}_3$  single crystal available in the literature. However, it must be taken into account that the residual carbon (C) on the film surface detected in the ESCA spectra, and pores observed by SEM, affect the refractive index value of the film prepared at  $250^\circ\text{C}$ . It is thought that these problems with this film may be overcome by furthermore improvement in control of the heat-treatment and partial hydrolysis conditions of the double alkoxide solution during the film preparation procedure. It seems possible that the preparation of  $\text{LiNbO}_3$  films with acceptable physical properties may be achieved with well-controlled processing even at a temperature as low as  $250^\circ\text{C}$ .

Fig. 7 shows the XRD pattern of stoichiometric  $\text{LiNbO}_3$  film, which exhibits preferred orientation to (006), crystallized at  $400^\circ\text{C}$ . Such a preferred oriented film was found to be crystallized by the heat treatment in a flow of water vapour and oxygen on a gel film, which was prepared with an underlayer of gel film using a diluted solution and then thickened by the multiple dip-coating. The crystallized film was confirmed to be epitaxial by the X-ray pole figure method. This processing is recommended as a promising method to prepare an epitaxial film at relatively low temperatures.

## 4. Conclusions

The study of the crystallization process of gel films was carried out to prepare epitaxial  $\text{LiNbO}_3$  films on sapphire (0001) substrates. The results are summarized as follows.

1. Epitaxial  $\text{LiNbO}_3$  films were prepared at  $400$  and  $500^\circ\text{C}$ . The formation of the underlayer of gel film from a dilute solution prior to multiple dip-coating is

TABLE II Refractive indices of the LiNbO<sub>3</sub> films determined by ellipsometry

Sample	Substrate	Refractive index
LN250 <sup>a</sup>	Sapphire (0001)	2.289
LN500 <sup>b</sup>	Sapphire (0001)	2.330
LiNbO <sub>3</sub>	(Single crystal)	2.2868

<sup>a</sup> LiNbO<sub>3</sub> film heat treated at 250 °C.

<sup>b</sup> LiNbO<sub>3</sub> film heat treated at 500 °C.

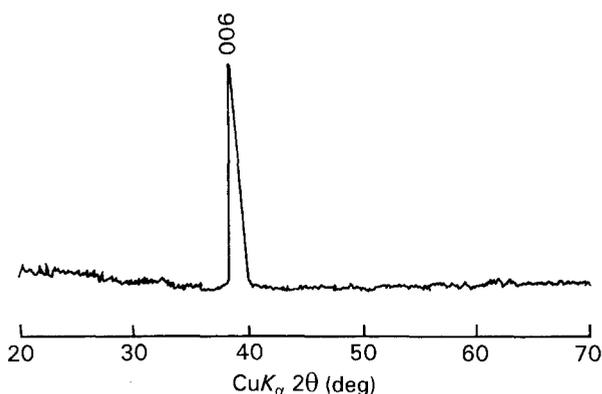


Figure 7 XRD profile of LiNbO<sub>3</sub> film prepared at 400 °C on sapphire (0001) with an underlayer film.

very favourable to achieve epitaxial growth of films to (006).

2. The depth profile of the chemical composition of the film revealed a chemical homogeneity comparable to that of single-crystal LiNbO<sub>3</sub>. The films prepared at 500 °C were homogeneous and smooth without any cracks or voids.

3. The Raman spectrum of the film prepared at 250 °C showed the initial state of the crystallization of

LiNbO<sub>3</sub>. The film crystallized at 500 °C exhibited Raman bands characteristic of the fundamental optical mode frequencies of single-crystal LiNbO<sub>3</sub>.

4. Refractive indices of the films were reasonable and comparable with that of single-crystal LiNbO<sub>3</sub>.

### Acknowledgement

This work was partly supported by Grant-in-Aid for Scientific Research on Priority Areas, The Ministry of Education, Science of Culture.

### References

1. S. HIRANO and K. KATO, *Adv. Ceram. Mater.* **2** (1987) 142.
2. *Idem, ibid.* **3** (1988) 503.
3. *Idem, J. Non-Cryst. Solids* **100** (1988) 538.
4. *Idem, Solid State Ionics* **32/33** (1989) 765.
5. S. HIRANO, K. KIKUTA and K. KATO, *Mater. Res. Soc. Sym. Proc.* **200** (1990) 3.
6. S. HIRANO, T. HAYASHI, K. NOZAKI and K. KATO, *J. Amer. Ceram. Soc.* **72** (1989) 707.
7. U. B. RAMABADRAN, H. E. JACKSON and J. T. BOYD, *Appl. Phys. Lett.* **58** (1991) 672.
8. R. F. SCHAUFLELE and M. J. WEBER, *Phys. Rev.* **152** (1966) 705.
9. A. S. BARKER Jr and R. LOUDON, *ibid.* **158** (1967) 433.
10. A. JAYARAMAN and A. A. BALLMAN, *J. Appl. Phys.* **60** (1986) 1208.
11. P. J. DELFYETT, R. DORSINVILLE and R. R. ALFANO, *Phys. Rev.* **B40** (1989) 1885.
12. J.-M. JEHNG and I. E. WACHS, *Chem. Mater.* **3** (1991) 100.
13. A. A. McCONNEL, *Spectrochim. Acta* **32A** (1976) 1067.

Received 23 June 1992  
and accepted 4 January 1993