Letter to the Editors

High-rate deposition of LiNb$_{1-x}$Ta$_x$O$_3$ films by thermal plasma spray CVD

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Abstract

LiNb$_{1-x}$Ta$_x$O$_3$ films were prepared by a thermal plasma spray CVD method using liquid source materials. Preferentially (0 0 1)-oriented LiNb$_{1-x}$Ta$_x$O$_3$ films with satisfactory in-plane and out-of-plane alignment were fabricated on sapphire (0 0 1) substrates. The full-width at half-maximum (FWHM) of the (0 0 6) rocking curve could achieve 0.12°, which was comparable with those of LiNbO$_3$ and LiTaO$_3$ films prepared by other conventional vapor-phase deposition methods. The deposition rate was up to 0.07 μm/min, which was 5–40 times faster than those for most other conventional vapor-phase deposition methods. From inductively coupled plasma atomic emission spectroscopy analysis, x values of these films were estimated to be 0.36–0.49. © 2000 Elsevier Science B.V. All rights reserved.

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Lithium niobate LiNbO$_3$ (LN), lithium tantalate LiTaO$_3$ (LT) and their solid solution lithium niobate–tantalate LiNb$_{1-x}$Ta$_x$O$_3$ (LNT) are highly promising materials in a variety of device applications such as optical waveguides, optical modulators, surface acoustic wave devices, second-harmonic generators and holographic memory. This is due to their interesting electrooptic, acoustooptic and nonlinear optical properties. Among these materials, LNT can be of a particular advant-age for some applications. Namely, the possibility to vary different thermal, optical and electrooptic properties, which are determined by the $x =$ Ta/(Ta + Nb) value, makes it a very attractive material [1]. A number of deposition methods for LN and LT films have been reported, including liquid-phase epitaxy (LPE) [2], molecular beam epitaxy (MBE) [3], pulsed laser deposition (PLD) [4], reactive sputtering [5] and metalorganic CVD (MOCVD) [6,7]. However, there have been only a few reports on LNT film deposition. Kawaguchi et al. [8] reported LNT film growth on LN substrates with x between 0 and 0.4, using the LPE method. In their experiment, film crystallinity (FWHM) degraded markedly when $x > 0.3$, corresponding to the increase of lattice mismatch and growth

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temperature. Recently, Cheng et al. [9] fabricated highly *c*-oriented LNT films with $x < 0.33$ on Si(1 1 1) substrates, using the sol–gel technique. They found that the degree of orientation was relatively low when $0.5 < x < 1$.

This is the first effort at depositing LNT films on sapphire, to our knowledge, even though sapphire has the same hexagonal (rhombohedral) symmetry and can be a very suitable substrate material for LNT films, because of its low refractive index and satisfactory geometric mismatches for hetero-epitaxy.

Since optoelectronic devices require films up to 100 μm thick, epitaxial thick film deposition techniques from the vapor-phase are highly anticipated. Thermal plasma spray CVD (TPS CVD) [10,11] is expected to be a promising candidate for epitaxial thick film deposition of multicomponent materials. This process has the following characteristics: (1) since composition-controlled high-temperature vapor can be generated, the preparation of multicomponent films may be easier; (2) any gas can be used as the plasma gas; (3) due to the high reactivity and the high particle density of a radio-frequency (RF) thermal plasma, high-rate deposition can be expected; (4) the use of a liquid raw material makes it easier to control the feeding rate of the source materials into the plasma continuously and accurately. In addition, the deposition species in the TPS CVD method are expected to be clusters, based on an analogy with the thermal plasma flash evaporation method, in which fine powders are employed as raw material [12,13]. In the thermal plasma flash evaporation method, high-rate deposition could be achieved because of the special role of nanometer-scaled clusters as deposition particles. Therefore, these features are thought to be advantageous for the high-rate deposition of multicomponent epitaxial thick films.

In the present study, we applied the TPS CVD method for the high-rate deposition of ferroelectric oxide LNT films, as the first step in the deposition of epitaxial thick films from liquid starting material.

Fig. 1 shows the TPS CVD apparatus, which is almost the same as the thermal plasma flash evaporation apparatus described previously [12,13], except for the liquid raw material feeding system,
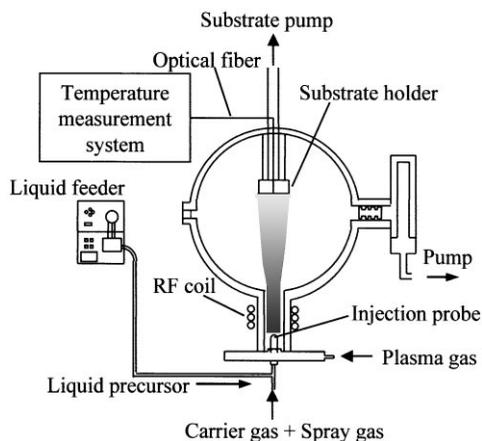

Fig. 1. Scheme of thermal plasma spray CVD apparatus used in present work.

additional substrate vacuum pump and induction coil for plasma generation. In this system, a plasma torch is set at the bottom of the chamber, and the plasma is blown upward to prevent large droplets of the liquid raw material from falling down. A liquid solution containing metalorganic precursors was fed into a RF O_2–Ar thermal plasma as a mist from the injection probe. The mist of sprayed solution was co-evaporated and oxidized completely and then deposited onto a substrate. The precursor source materials were introduced into the plasma using a liquid feeder utilizing a pump with a feeding rate (R) of 1 ml/min. The substrate temperature was controlled within the accuracy $\pm 15°$C and was measured by detecting infrared radiation from the reverse side of the substrate through an optical fiber, which made it possible to monitor the substrate temperature directly in real time. The torch-substrate distance was varied between 300 and 370 mm. Carrier argon gas (3 l/min), inner argon gas (3–5 l/min) and spray argon gas (2.6–3.8 l/min), along with tangential oxygen gas (45 l/min), were introduced into the chamber through and around the injection probe. The total pressure in the chamber was maintained at 150 Torr. Lithium–niobium and lithium–tantalum alkoxide metalorganic solutions commercially available for dip coating [LiNb(OR)$_6$ and LiTa(OR)$_6$ in 3-methylbutyl acetate as a solvent, Kojundo Chemical Lab. Co., Japan] were used as

liquid precursors. The concentration of metals (Li and Nb or Li and Ta) in individual precursor solutions, which were then mixed in appropriate ratios, corresponded to 3 wt% $LiNbO_3$ and 3 wt% $LiTaO_3$, respectively. In this study, two types of mixtures with Nb : Ta ratios of 1 : 1 and 3 : 2 were used as initial materials. Optically polished sapphire (0 0 1) single-crystal plates (10 mm × 10 mm × 0.5 mm in size, Earth Chemicals Ltd., Japan) were used as substrates.

Film thickness was examined by scanning electron microscopy (SEM). The crystallinity, phase and orientation of the films were determined by X-ray diffraction (XRD) using θ–2θ and θ modes and pole figure X-ray measurement. The composition of the films was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

On sapphire (0 0 1) substrates, mirror-like and transparent films could be grown under all conditions employed in this experiment. From the cross-sectional SEM images, the deposition rate was estimated to be between 0.04 and 0.07 μm/min (2.4–4.2 μm/h), which is about 5–40 times faster than those of many other conventional deposition methods for LN and LT films [14].

According to ICP-AES data, from the two precursor mixtures with the Nb : Ta ratios of 1 : 1 and 3 : 2, two series of $LiNb_{1-x}Ta_xO_3$ films with x equal to 0.45–0.49 and 0.36–0.41, respectively, were prepared. The c parameters for LNT films calculated from the XRD patterns were equal to 13.75–13.77 and 13.77–13.79 Å for the films with x = 0.45–0.49 and 0.36–0.41, respectively, which are in good agreement with the results of ICP-AES measurements, since a more Ta-rich material should show a smaller c parameter. According to JCPDS data for bulk materials, this parameter decreases from 13.862 Å for LN via 13.815 Å for $LiNb_{0.5}Ta_{0.5}O_3$ to 13.755 Å for LT. Somewhat smaller c lattice parameters of LNT films compared to those for bulk materials can be ascribed to compression along the c-axis and consequent extension in the (0 0 1) plane. These are due to a large lattice mismatch and a large difference between the thermal expansion coefficients of LNT and sapphire. As was indicated previously [4], the misfit parameter between LN film and z-cut sapphire substrate is

7.7% at room temperature and becomes equal to 8.6% at the $T_{sub} = 750°C$.

The effect of the substrate temperature (T_{sub}) and torch substrate distance (L) on the crystalline orientation of the films at a feeding rate (R) of 1 ml/min between 650 and 810°C was studied. Under conditions employed in this study, the distance L did not significantly influence film orientation; the role of the T_{sub} parameter was more important. The XRD patterns at T_{sub} above 750°C usually exhibited a strong (0 1 2) peak, along with a (0 0 6) peak. Below this temperature, highly or almost completely (0 0 1) oriented films could be obtained. A similar influence of T_{sub} on the orientation of LN films on silica substrates was reported by Wu et al. [15]. Lee and Feigelson [16] also varied the texture direction of their LN films on SiO_2/Si substrates from (0 0 6) to (0 1 2) by increasing the T_{sub} parameter or by decreasing the growth rate. They inferred that the gradual change in texture from the (0 0 6) to the (0 1 2) direction at higher temperatures might be explained in terms of surface free energy anisotropy. As T_{sub} increases, adspecies can attain sufficient surface mobility to arrange themselves into grains with the lowest surface energy (0 1 2) planes parallel to the surface. At increased growth rates, the formation of (0 1 2) orientation was observed at a higher growth temperature, since in this case adspecies could not diffuse farther along the growth interface to form energetically favorable sites with reduced surface energy [16]. In our experiments both the growth rate and the temperature, at which the change in texture direction was observed, were higher, and this is well consistent with the above explanation.

Fig. 2(a) shows the XRD pattern of the LNT film with almost complete (0 0 1)-orientation, deposited at $T_{sub} = 710°C$ and L = 350 mm for 5 min. This figure indicates that the film is mainly composed of grains whose c-axis is perpendicular to the film surface. Between the various possible textures, this is the most attractive LNT waveguide structure, because of its higher electrooptic and nonlinear optical coefficients along this direction. The surface morphology of this film is given in Fig. 2(b). As estimated by cross-sectional SEM analysis, its thickness was about 0.24 μm, the x = Ta/(Ta + Nb) value was equal to 0.49, and the
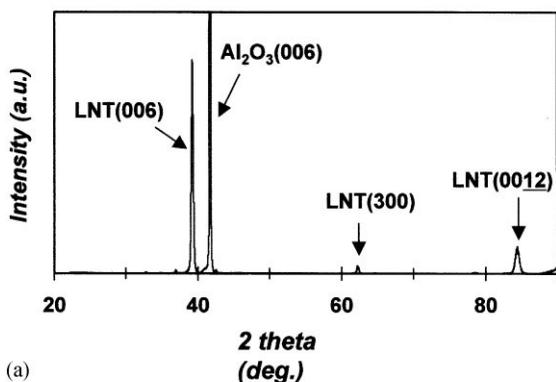
(a)
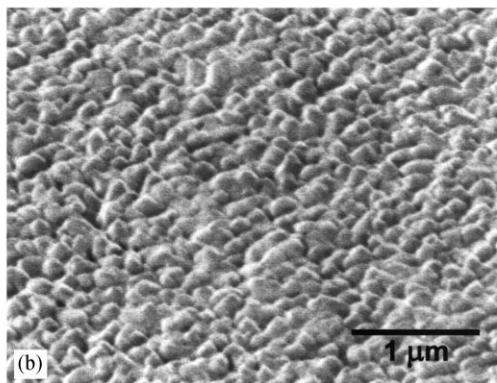
(b)

Fig. 2. XRD pattern (a) and SEM surface image (b) of the LiNb$_{1-x}$Ta$_x$O$_3$ film ($x = 0.49$) on sapphire (0 0 1) substrate. The film was deposited at $T_{\text{sub}} = 710°$C and $L = 350$ mm for 5 min.

FWHM of the (0 0 6) rocking curve was equal to 0.31°.

The narrowest (0 0 6) rocking curve FWHM of LNT film was achieved at a high deposition temperature $T_{\text{sub}} = 750°$C and $L = 320$ mm for 5 min and was equal to 0.12°, which was comparable to the values reported for LN and LT films deposited by other conventional vapor-phase methods. It was impossible to improve this FWHM value using a higher deposition temperature, because above $T_{\text{sub}} = 750°$C, a significant number of grains with (0 1 2) orientation appeared, which decreased the film crystallinity due to higher grain boundary stress. This film was grown using Nb-rich initial solution (Nb:Ta = 3:2), and therefore its $x =$ Ta/(Ta + Nb) was about 0.40, whereas its thickness was estimated to be 0.30 μm. The relation between the crystal axes of this film and the in-plane vectors

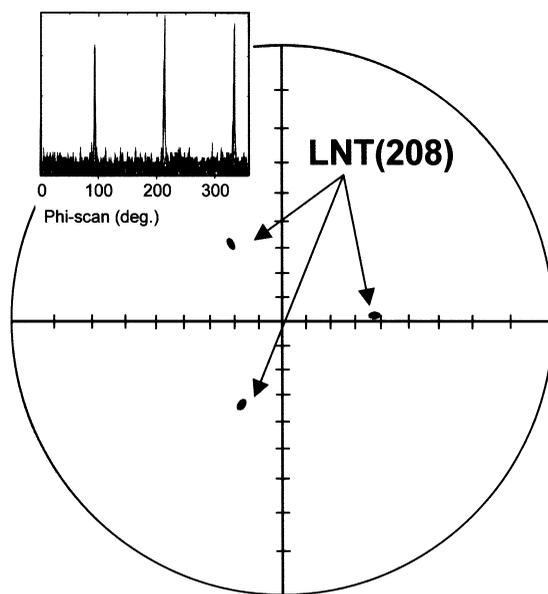Fig. 3. X-ray pole figure of the LiNb$_{1-x}$Ta$_x$O$_3$ film ($x = 0.40$) deposited at $T_{\text{sub}} = 750°$C and $L = 320$ mm for 5 min; normals of LiNb$_{1-x}$Ta$_x$O$_3$ (2 0 8) planes are indicated. The inset shows XRD ϕ-scan result for the (2 0 8) planes.

of the sapphire substrate was obtained from an X-ray pole figure. Fig. 3 shows only one group of LNT (2 0 8) poles. This suggests that c-oriented film is grown with epitaxial orientation and there is no evidence of twins, which are rotated by 60° and are common for many deposition techniques for LN and LT films [4,6,14,17]. However, most of other films prepared at lower T_{sub} contained some fraction of twinned grains.

In conclusion, preferentially (0 0 1)-oriented LiNb$_{1-x}$Ta$_x$O$_3$ films were prepared on sapphire (0 0 1) substrates by the thermal spray plasma CVD method using a liquid source material. The FWHM of the (0 0 6) rocking curve could achieve 0.12°, revealing satisfactory out-of-plane orientation. Good epitaxial orientation of LNT films was confirmed by pole figure measurements. The deposition rate of approximately 0.07 μm/min was 5–40 times faster than those of other conventional vapor-phase deposition methods, and LNT films over 0.5 μm thick could be prepared by 10 min deposition. From ICP-AES analysis, x values of these films were estimated to be 0.36–0.49,

depending on the Nb/Ta ratio of the starting source liquid mixture.

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