EPITAXIAL GROWTH AND OPTICAL PROPERTIES OF SOL-GEL $(Pb,La)TiO_3$ THIN FILMS FOR WAVEGUIDES

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ABSTRACT

Lead lanthanum titanate thin films have been prepared on MgO and sapphire substrates by sol-gel method. XRD analyses confirm that the PLT films fabricated on MgO(100) and c-plane sapphire substrates grow preferentially with (100) and (111) orientations, respectively. The PLT films with a high La content have a low refractive index due to the decrease of the refractive index anisotropy. The propagation losses in PLT films measured, using He-Ne laser light and the prism coupling method decrease as the La content increases. This is due to the reduction of the refractive index anisotropy and the surface scattering by the surface roughness as a function of La content in the film.

INTRODUCTION

Lanthanum-modified lead zirconate titanate ($(Pb,La)(Zr,Ti)O_3$, which is called PLZT) system is a well known ferroelectric material. Since PLZT is transparent in the visible and near-infrared region, as well as having excellent electro-optic characteristics, it has been known as a potential candidate for excellent optical waveguide applications [1,2]. For electro-optic application, it is very important to prepare high-quality epitaxial thin films to take the advantage of anisotropic properties of the ferroelectric materials. Specially, the composition without zirconium content ($(Pb_{1-x}La_x)Ti_{1-x/400}O_3$, which is called PLTx) has been known to be more adequate for waveguide applications due to its finer grain size and higher transparency than PLZT [3]. PLT thin films for optical waveguide applications must have grain sizes smaller than the operating wavelength, higher refractive index than that of the substrates, thickness range between 0.2-1.0 μm, absence of the defects and optical inclusions, and crystallographic orientation or epitaxy [4]. Recently, sol-gel processing of the PLZT thin films has been extensively studied due to the advantages such as precise composition control and homogeneity, low temperature synthesis, large-area deposition, low cost, and fast fabrication process.

In this study, highly oriented PLT thin films were prepared on various single crystal substrates such as MgO and sapphire by sol-gel process, and the optical properties such as the refractive index, and the optical propagation loss of the films were measured as a function of La content.

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EXPERIMENT

Thin Film Preparation

The procedure for preparing the precursor solution is shown in Fig. 1. 5 mole % excess Pb was incorporated since it was found that excess PbO aids significantly to compensate for PbO losses. The solutions were spin-coated on a substrate using a spin coator (Headway Research Inc., EC101-R485) at 1500 rpm for 30 secs. The selection of the substrates is very important for the epitaxial growth of the thin film, since the lattice parameter and the crystal structure matching between the film and the substrate drastically affect the growth behavior of the film. Considering the lattice matching, MgO(100) and c-plane sapphire single crystal substrates which were double-side polished for optical experiments, were used in this study. Then the green films were dried at 400°C on hot plate for 10 mins., yielding about 500 Å thickness per a coating. This procedure was repeated until a desired thickness was obtained. The films were heat-treated with 5°C/min. to 700°C holding for 30 mins. to crystallize them. And all the films were cooled at 2°C/min. in atmosphere to prevent formation of microcracks from thermal shock during the cooling step.

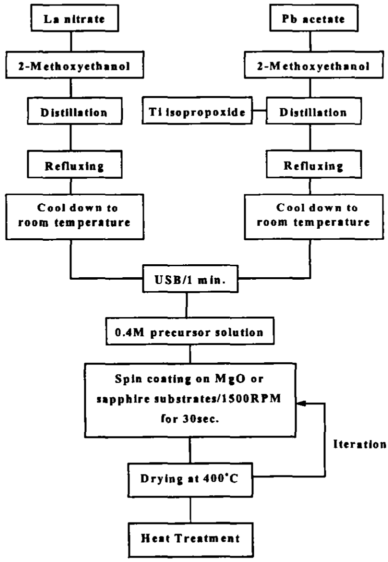

Fig. 1 Flow chart for preparation of PLT solution and thin films.

Characterizations

The crystalline phase and the crystallographic orientation of the PLT film fabricated on MgO and sapphire substrates were examined using X-ray diffraction (Rigaku, D/MAX-RC). The RMS surface roughness of the films were determined using an atomic force microscope (Park Scientific Instruments, Autoprobe 5M). In order to measure the refractive indices and propagation losses of the films, the prism coupling method was used.

RESULTS AND DISCUSSION

Preparation of PLT Thin Films

XRD patterns of the PLT5 films fabricated on MgO(100) and c-plane sapphire substrates, for several the film thicknesses are shown in Fig. 2. All the films showed single perovskite phase without any other noticeable phases. In Fig. 2(a), PLT thin films are preferentially a-axis oriented, and the intensity of main peaks is enhanced compared to those of the extra peaks of (110) and (111) as the number of coatings is increased. However, the extra peaks increase gradually with increase in the thickness of the film. The enhancement of the crystallization with increasing film thickness produce the highly orientation of (100) plane. On the other hand, since the thicker film over the critical film thickness makes the bulky film having nonuniformity, it promote the growth of the extra peaks of (110) and (111) planes preventing the nucleation of main peak of (100) plane. Fig. 2(b) shows that PLT films are grown highly (111)-oriented on sapphire substrates. The XRD pattern dependence on the film thickness is similar to that of PLT films on MgO substrate. For low film thickness, the intensity of main (111) peak increases with increasing the film thickness, but the extra peaks of (100), (200) and (110) planes increase gradually with increase in the film thickness .

XRD patterns of the PLT films (3500Å thick) fabricated on MgO and sapphire substrates having different La content are shown in Fig. 3. For the films on MgO substrate, main (100) and (001) peaks are observed for low La content, but only (100) peak is detected when La content is more than 20 mole % as shown in Fig. 3(a). As La content in the film increases, the tetragonality of PLT perovskite structure decreases. That is, the tetragonal structure of PLT films changes to cubic structure in the film [5]. (111) peak is dominant regardless of La content in the film for the films on sapphire substrate, as shown in Fig. 3(b). Also, the intensity of main (111) peak increases and reduction in the distance between the (111) peak of the PLT film and the (0001) peak of the sapphire substrate is observed with increasing La content. We ascribe this to improved lattice match between (111)-oriented PLT film and c-plane sapphire substrate, due to the change from tetragonal structure to cubic structure in the PLT films with increasing La content in the film.

The rocking curves for the PLT films on MgO and sapphire substrates are shown in Fig. 4. The full-widths-at-half-maximums (FWHM) of the x-ray rocking curves are about 4.5 and 0.3 for the films on MgO and sapphire, respectively. However, the variation of FWHM as a function of La content is not found for all the PLT films on same substrate. We speculate that PLT films on sapphire substrates have better alignment than those on the MgO substrate.

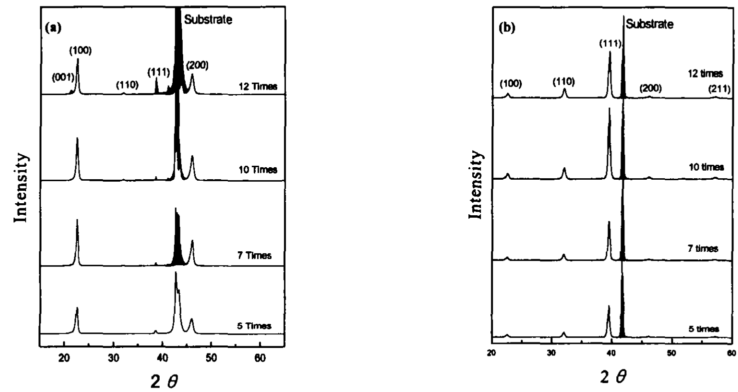

Fig. 2 XRD patterns of PLT films on (a) MgO and (b) sapphire substrate as a function of the film thickness.

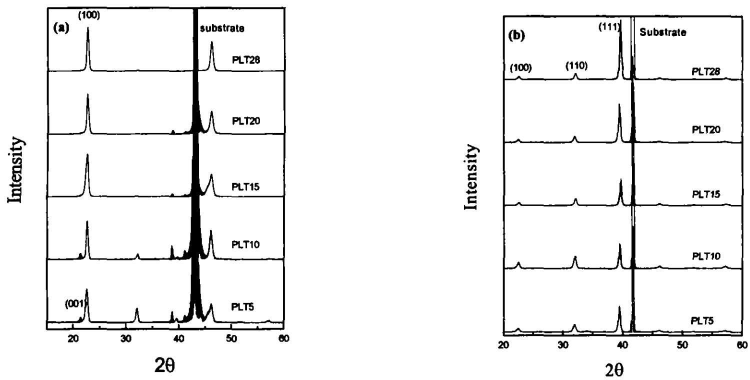

Fig. 3 XRD patterns of PLT films on (a) MgO and (b) sapphire substrate as a function of La content.

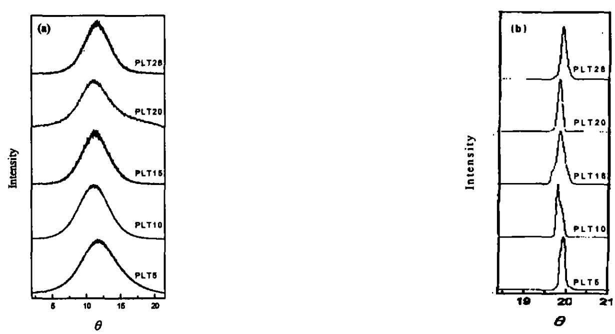

Fig. 4 Rocking curves for (a) (100) PLT on MgO and (b) (111) PLT on sapphire substrate.

In order to obtain epitaxial or highly oriented films, it is desirable that most nuclei be formed at the interface between the film and substrate, and the lattice of the substrate should match with the film. When the processing temperature is high, heterogeneous nucleation of perovskite grain at the interface between the film and the substrate occurs easily. Therefore, the processing temperature used in this study was 700°C, which is 150°C higher than the crystallization temperature obtained by DTA and TG.

Optical Properties of PLT Films

The refractive index of the film as a function of La content, measured by the prism coupler, is shown in Fig. 5. The refractive index of the films on MgO substrate decreases with increasing La content, dropping from 2.34 to 2.15. As La content increases, the tetragonality of the PLT film decreases causing the reduction of the anisotropy in the refractive index. Thus, the average refractive index decreases with increasing La content since the refractive index for the light polarized parallel to the c-axis, which is higher than that along the a-axis, decreases. However, in the case of the polycrystalline PLT film on glass substrates, the reduction of the refractive index is small since these films are randomly oriented.

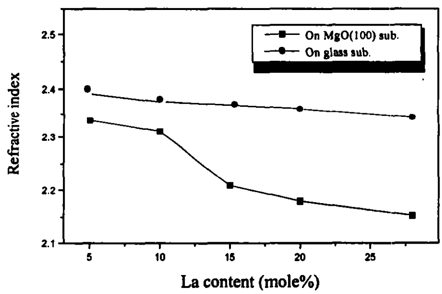

Fig. 5 Refractive indices of PLT films fabricated on MgO and glass substrates as a function of La content.

The optical propagation losses of the PLT films on MgO and sapphire substrates as a function of La content are plotted in Fig. 6. The propagation losses decrease with an increase in La content due to the reduction of optical scattering. According to AFM analyses, the RMS surface roughness of PLT films decreases linearly from 46Å to 15Å with a increase of La content as shown in Fig. 7. This is due to being the grain size smaller for higher La content composition. Thus, the propagation losses decrease as La content increases due to the reduction of the refractive index anisotropy as well as of the surface scattering by the surface roughness as a function of La content.

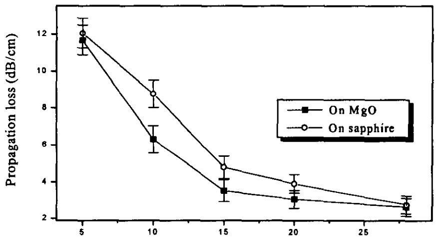

Fig. 6 Propagation losses of PLT films fabricated on MgO and sapphire substrates as a function of La content.

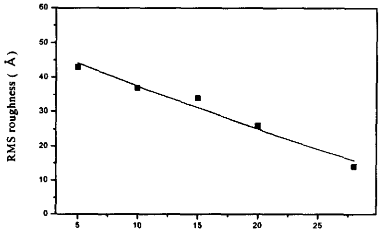

Fig. 7 RMS surface roughness of PLT films on MgO substrate depending on La content.

SUMMARY

Highly oriented PLT thin films are prepared on MgO(100) and c-plane sapphire substrates by sol-gel method. The films are heat-treated at 700°C which is 150°C higher than the crystallization temperature for 30 min. to enhance the heterogeneous nucleation at the interface between the film and the substrate. Although the PLT films fabricated on MgO and sapphire substrates have (100) and (111) orientations respectively, the epitaxy of the films was affected by the film thickness and the composition. As La content increases, the tetragonality of perovskite structure as well as the anisotropy of refractive index decrease and the film surface becomes smoother. Thus, the refractive index and the propagation loss of the film decrease with increasing La content.

ACKNOWLEDGMENTS

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