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Preparation and properties of two-dimensional PLZT photonic crystals using a sol–gel method

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Abstract

Lead lanthanum zirconate titanate (PLZT) film with an array of air-holes was successfully fabricated on a platinum-deposited (0 0 1) magnesium oxide substrate using a sol–gel method with a resist mold. A PLZT precursor solution was cast into a mold with resist pillars patterned using electron-beam lithography. After removing the resist pillars and applying a firing process, a PLZT ceramic film with air-holes was obtained. The patterned PLZT film was grown epitaxially on the substrate. Reflection peaks were also observed by optical measurement of PLZT film with a hexagonal array of air-holes. The frequency range of the reflection peaks coincided with that of the calculated photonic band structures. We consider that this periodic structure and process are suitable for preparing tunable photonic crystals.

Keywords: Sintering; Sol–gel processes; Optical microscopy; Optical properties; PLZT

1. Introduction

Since the concept of photonic crystals (PCs) was originally proposed,[1] they have attracted much attention because of their potentially wide range of applications, particularly in novel optical devices. PCs are artificial structures that have a periodically modulated refractive index and they are designed to control photons in the same way that crystals in solids control electrons. The photonic band structures in a PC are defined by parameters such as the refractive index (dielectric constant) of the material forming the PC, the period, and the shape of the periodical array. Some PCs have a photonic band-gap (PBG) that prevents propagation of light within certain frequency ranges. Other unique properties have been reported including an extraordinary angle-sensitive light propagation (the superprism phenomenon in PCs).[2] PCs are also likely to have novel applications in telecommunications systems in the form of extremely small planar light-wave circuits, optical add-drop multiplexers/demultiplexers, or as dispersion compensators for wavelength-division multiplexing communication systems.

Semiconductor materials such as Si, AlGaAs, InP, etc. have often been chosen for fabricating PCs because they have high refractive indices and transparency in the wavelengths used for telecommunication. However, PCs made from these semiconductor materials seems to be difficult to tune their photonic band structures at very high speed in order to deal with signals in telecommunications systems. The tunability of these structures at very high speed is likely to be a very useful additional function in a number of applications.

Lead lanthanum zirconate titanate (PLZT) has been used for a range of electro-optic devices, including optical waveguides, optical modulators, and optical shutters, because of its high transparency and excellent electro-optic properties. In particular, $Pb_{0.865}La_{0.09}Zr_{0.65}Ti_{0.35}O_3$ (PLZT (9/65/35)) has small remanence and nearly anhysteretic polarization with changes in the electric field. This slim ferroelectric hysteresis loop may be suitable for continuous device applications. Furthermore, PLZT (9/65/35) exhibits excellent quadratic electro-optic effects.[3] The speed of the changes

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in the refractive indices induced by electro-optic effects are very fast. The behavior of light with a frequency near that of the PBGs is thought to be controlled at very high speed. Recently, Li et al.[4] showed that inverse opals consisting of ferroelectric PLZT (9/65/35) materials had tunable photonic band structures driven by an external electric field. The refractive index of the inversed opals was modulated in three-dimensional (3D) directions. However, two-dimensional (2D) PCs are also thought to be useful because they require a lower driving voltage to tune the photonic band structures.

We considered that epitaxial PLZT films would have a low leakage current and high transparency. And, a sol–gel method has the advantages of high purity, high controllability of composition, and low processing temperature. In this paper, we therefore investigated the feasibility of using a sol–gel method with an electron-beam (EB) resist mold to fabricate epitaxial PLZT 2D-PCs with photonic band structures.

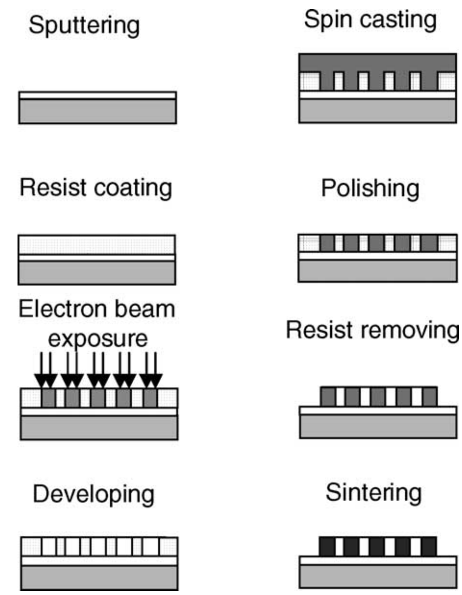

Fig. 1. Schematic illustration of preparation of samples using sol–gel method with resist molds.

2. Experimental procedure

Fig. 1 shows a schematic of the preparation process using the sol–gel method with a resist mold. First, a 30-nm-thick Pt layer was deposited on (0 0 1) single crystalline magnesium oxide (MgO) substrates at 400 °C using a radio-frequency magnetron sputtering apparatus (SH-350E, ULVAC, Japan). Next, a 700-nm-thick EB resist was coated on the Pt-sputtered (0 0 1) MgO substrate (Pt/MgO) using a spin-coating method. Square and hexagonal arrays of resist pillars were produced using an EB lithography system (ELS-5700, Elionix, Japan, or JBX7000SB, JEOL, Japan). The period and radius of the resist pillars were 1000 and 150 nm for the square arrays, and 400 and 100 nm for the hexagonal ones, respectively. The drawing areas were about 7 mm × 10 mm for the square arrays and for 10 μm × 2 mm the hexagonal ones. A PLZT (9/65/35) precursor solution with 10 mol% excess PbO was cast into the resist molds by spin coating. After baking at 130 °C on a hot plate for 5 min in air, the molds were completely filled with the PLZT precursor. The overflow of the gel layer was removed by mechanical polishing and the samples were baked again at 180 °C on a hot plate for 5 min in air to reinforce the patterned gel. After the resist molds were removed by a chemical solution, the patterned PLZT precursor films were pyrolyzed at 400 °C for 5 min in air and sintered at 725 °C for 1 min in air.

The microstructure of the PLZT films with arrays of air-holes was observed with a scanning electron microscope (SEM) and the crystal structure of the films was analyzed by X-ray diffraction (XRD), θ–2θ scanning and ϕ scanning measurements using Cu Kα1 radiation.

We carried out optical reflectance measurements using the method reported by Poborchi et al.[5] to confirm that there were PBGs in the PLZT PCs. A microscope, with a tungsten lamp as a light source, and an objective lens (magnification: ×50) were used. As incident light within the same frequency range as the PBGs cannot propagate in PCs, most of the light should be reflected. Thus, strong reflection was observed near the PBG frequencies. The samples were cleaved to have a facet surface perpendicular to the Γ–M and Γ–K direction in the Brillouin zone corresponding to the unit cell of the PC with a hexagonal array. Incident light was irradiated on to the cleaved facets and the reflection was measured using a spectroscopy system. The range of the wavelength

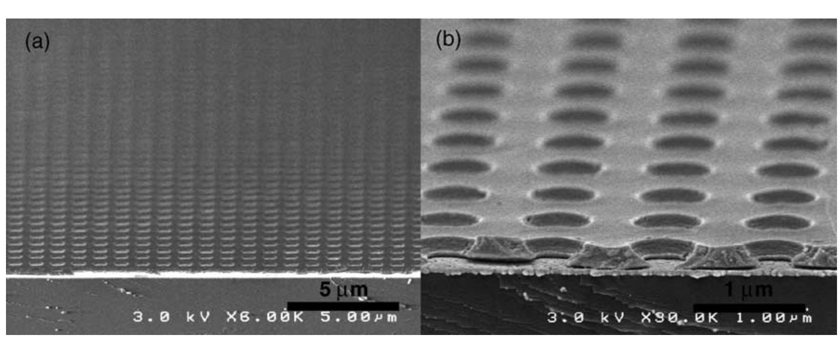

Fig. 2. SEM images of PLZT films with square array of air-holes with period of 1000 nm and radius of 250 nm.

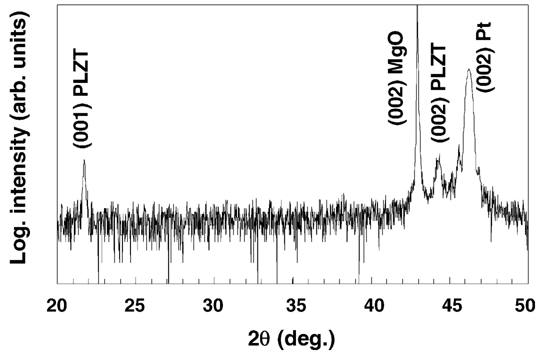

Fig. 3. XRD θ–2θ spectrum of PLZT film with square array of air-holes with period of 1000 nm and radius of 250 nm/Pt/(0 0 1) MgO.

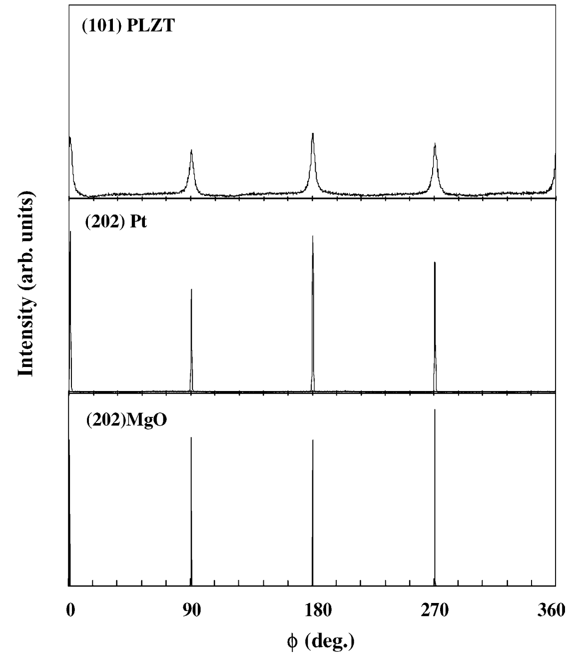

Fig. 4. XRD ϕ-scan measurements of PLZT film with square array of air-holes with period of 1000 nm and radius of 250 nm/Pt/(0 0 1) MgO.

investigated was 400–1000 nm. To analyze the reflectance spectra obtained from the patterned PLZT film, an MIT Photonic Band Gap package was used. We assumed that the PC was perfectly two-dimensional, and that the refractive index for the PLZT was 2.5.

3. Results and discussion

Fig. 2 shows SEM images of the square array of a PLZT film with air-holes. These figures clearly indicate that PLZT films with an array of air-holes on the substrates were obtained using this sol–gel method with resist molds. The radius of the air-holes of the square arrays was 250 nm, because of heat treatment. Although the thickness of the films decreased after heat treatment to around 200 nm, the shape of the air-holes was maintained with no cracks.

We investigated the crystallinity of the PLZT film with square arrays of air-holes. The XRD θ–2θ spectrum of the patterned PLZT film is shown in Fig. 3. $\{0\,0\,1\}$ peaks appeared, but no other peaks from the PLZT (perovskite phase) and Pt were found on the MgO substrate, indicating that the unit cells of the patterned PLZT and Pt were *c*-axis oriented. Fig. 4 shows the XRD ϕ-scan spectra of the patterned PLZT, Pt layer, and MgO substrate. The peaks obtained emerged at nearly the same azimuth angle as the substrate reflections and were 90° apart. The fourfold symmetry of each layer indicated that the patterned PLZT and Pt layer were epitaxially grown on the (0 0 1) MgO substrate.

Fig. 5(a) shows an SEM image of the top view of a PLZT film with a hexagonal array of air-holes with a period of 400 nm and radius of 135 nm. The Γ–M and Γ–K directions, which were tied to symmetry points in the Brillouin zone corresponding to the hexagonal array, are shown in Fig. 5(b). The in-plane reflection spectra for the PLZT film with a hexagonal array of air-holes with incident light along the Γ–K and Γ–M direction for both transverse electric (TE) and transverse magnetic (TM) polarization are shown in Fig. 6(a) and (b). The light frequencies were normalized by the period of the hexagonal array. The reflectivity peaks that we obtained were normalized by their backgrounds. Along the Γ–K direction, no obvious peaks were detected for TE and

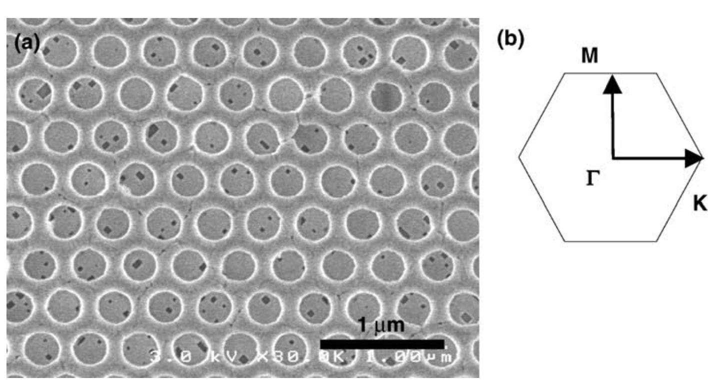

Fig. 5. (a) SEM image of top view of PLZT films with hexagonal array of air-holes with period of 400 nm and radius of 135 nm; (b) 2D Brillouin zone corresponding to hexagonal array and symmetry points.

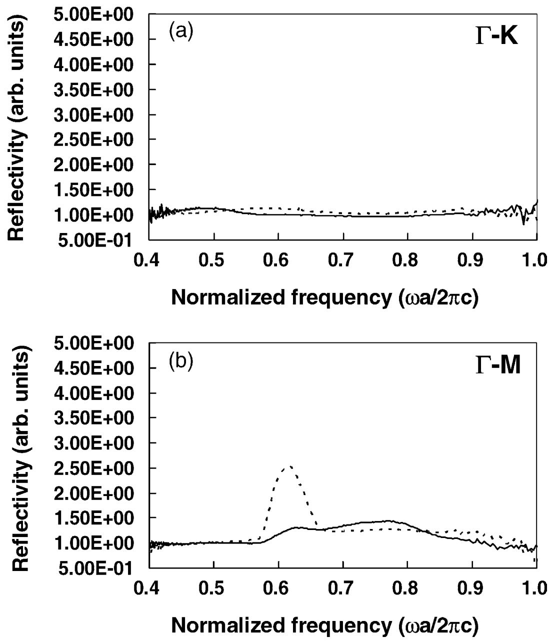

Fig. 6. Experimental reflection spectra of PLZT PC shown in Fig. 5 for (a) Γ–K direction, (b) Γ–M direction. Solid and dotted lines indicate TE and TM polarization, respectively.

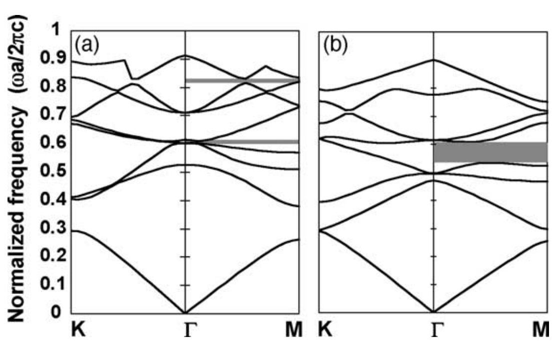

Fig. 7. Calculated photonic band structures for PLZT photonic crystal in ideal 2D case for TE mode (a), TM mode (b); grey areas indicate expected PBG.

TM polarization. In contrast, along the Γ–M direction, an obvious peak for TM polarization and vague peaks for TE polarization were observed. For TM polarization, the reflection peak appeared in the frequency range from 0.57 to 0.67. However, for TE polarization, it was difficult to determine the range of frequencies; the center of the peaks may have been around 0.65 and 0.78.

The photonic band structures in the patterned PLZT film were calculated using the values of the period and radius. The results of calculations of the hexagonal array for the TE and TM modes in the patterned PLZT film are shown in Fig. 7(a) and (b), respectively. The gray areas in the figures represent the calculated PBG of the arrays for each direction and polarization. The calculated PBGs were produced only along the Γ–M direction for both TE and TM polarization. The frequency ranges of the calculated PBGs were 0.60–0.61and 0.82–0.83 (for the TE modes) and 0.54–0.61 (for the TM modes), respectively.

A comparison of the frequency ranges of the experimental reflection spectra and those of the calculated PBGs showed that there were still small differences between the values of the frequencies. To calculate them more accurately, we will have to consider other parameters including the refractive index and surface plasmon of the thin Pt film, and the thickness of the PLZT patterned film. However, we believe that the reflection spectra obtained for the patterned PLZT films can be interpreted as indicating that PBGs formed in the crystals.

4. Conclusion

Lead lanthanum zirconate titanate (PLZT) films with arrays of air-holes were successfully fabricated on platinum-deposited (0 0 1) magnesium oxide substrates using a sol–gel method with a resist mold. A PLZT precursor solution was cast into a mold with resist pillars patterned using electron-beam lithography. After removing the resist pillars and applying a firing process, PLZT ceramic films with air-holes were obtained. The patterned PLZT film was grown epitaxially on the substrate. Reflection peaks were also observed by optical measurement of a PLZT film with a hexagonal array of air-holes. The frequency ranges of the reflection peaks coincided with those of the calculated photonic band structures. We believe that this periodic structure and the process used are suitable for preparing tunable photonic crystals.

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