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Preparation and Optical Properties of PLZT Single Crystalline Thin Films

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Single crystalline PLZT thin films were grown epitaxially on single crystals of sapphire, $SrTiO_3$ and spinel by rf-sputtering. Crystallinity of the film was studied using X-ray and reflection electron diffraction. The band gap of PLZT was determined to be 2.8 eV. The refractive index is measured using the m-lines method. Based on the analysis of dispersion in refractive indices, the dispersion parameter for single crystalline PLZT is determined to be $6.23 \sim 6.35 \times 10^{-14}$ eVm.^{2} The attenuation constant of about 10 db/cm was obtained for He-Ne laser light in the PLZT thin film light waveguide on sapphire.

§1. Introducton

Ferroelectric ceramics PLZT, [(Pb, La) (Zr, Ti)O_3], are transparent in the visible and infrared regions, and have large electrooptic effects[1)] as single crystalline electrooptic materials like $LiNbO_3$ and $LiTaO_3$. Various applications for erasable image storage devices and light valves using PLZT transparent ceramics have been proposed.[2)] Samples with adequate thickness for such devices are usually made by polishing ceramics prepared by hot-pressing technique or by sintering in PbO atmosphere. For application, however, it is desirable to obtain thin films of PLZT without techniques of hot-pressing and subsequent polishing. The authors have established the method to prepare PLZT thin films by rf-sputtering,[3,4)] and reported dielectric,[4,5)] optical,[5,6)] and electrooptic properties[6,7)] of the films. Single crystalline PLZT can be epitaxially grown on various single crystalline substrates.[8,9)]

In this paper, crystallinitity of the epitaxially grown PLZT single crystalline thin films is described, and optical properties of the films are reported. Some physical constants of single crystalline PLZT are elucidated using the observed optical properties. A new application of PLZT thin films is proposed.

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§2. Epitaxial Growth

Single crystalline PLZT thin films were grown by rf-sputtering using a powder target of sintered PLZT. The mole fraction (La/Zr/Ti) of the target powder is 9/65/35. The powder container of 80 mm in diameter was made of a titanium (Ti) plate. Wafers of (0001) sapphire (α-Al_2O_3), (100) strontium titanate ($SrTiO_3$) and (100) spinel ($MgO \cdot Al_2O_3$) were used as substrates. Some physical constants of PLZT and the substrate materials are listed in Table I. Mirror-polished substrates of $0.3 \sim 0.5$ mm in thickness were soaked in dilute alkaline solution and then rinsed in deionized water. The sputtering condition was as follows: anode voltage of 1.8 kV, anode current of 180 mA, input rf power of 180 W, Ar/O_2 gas ratio of $90/10 \sim 50/50$, and total gas pressure of 7×10^{-2} Torr. Substrate temperature was kept above 700°C. The growth rate of the epitaxial PLZT layer was $60 \sim 80$ Å/min when the substrate and the target are put with a distance of 3.5 cm.

The composition of the PLZT thin films was found to be very close to that of the target by using Auger Electron Spectroscopy. The depth profile of the Auger signal obtained by ion milling technique shows the uniform composition along the film thickness.

Crystal structure and growth orientation were studied using X-ray diffraction and reflection electron diffraction method.[8,9)] The (111) plane of PLZT grows on the (0001) plane of sapphire, and the (100) plane of PLZT on the

Table I. Physical Constants of PLZT and Substrate Materials

material	PLZT (9/65/35)	sapphire (α-Al_2O_3)	$SrTiO_3$	spinel ($MgO \cdot Al_2O_3$)
structure	pseudo cubic (perovskite)	rhombohedral (α-Al_2O_3)	cubic (perovskite)	cubic (spinel)
lattice const. (Å)	4.08	$a=4.76$ $c=12.99$	3.90	8.02
refractive index (at 0.63 μm)	2.5	$n_0=1.765$ $n_e=1.757$	2.378	1.714

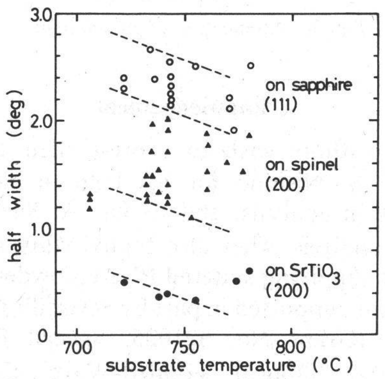

Fig. 1. Half width of X-ray rocking curves for the films on various substrate materials against substrate temperature.

(100) planes of $SrTiO_3$ and spinel. The crystallinity of the PLZT films can be evaluated using X-ray rocking curves which were taken by fixing the angle of the 2θ axis of a diffractometer at the main diffraction peak and scanning the angle of the θ axis. The (111) diffraction peak of PLZT film on sapphire and (100) on $SrTiO_3$ and spinel were studied. In Fig. 1, the half widths of the rocking curves are shown against the substrate temperature. The half width is smaller for the PLZT film on $SrTiO_3$ substrates compared with that on the other substrates because of the small lattice mismatch as in Table I. The half width becomes small when the substrate temperature becomes high, which implies that the crystallinity of the film is improved by increasing the substrate temperature.

§3. Optical Properties

The transparency of the single crystalline PLZT film is as high[5,6] as that of transparent ceramics. The photon energy dependence of the absorption coefficient of the PLZT film was calculated from the transmittance and reflectance of the film. The absorption coefficient remarkably decreases below the photon energy of 2.8 eV, which indicates the optical absorption edge to be about 2.8 eV.

The refractive index and the film thickness of the PLZT film could be accurately determined by the m-lines method[10] with He-Ne laser light of 6328 Å. Using interference fringes in transmittance or reflectance curves in the range of 350 nm$\sim$2 μm and the accurate film thickness determined above, the wavelength (λ) dependence of the refractive index (n) was obtained. The dependence is well explained by the following single term Sellmeier dispersion formula:[11]

$$n^2-1=S_0\lambda_0[1-(\lambda_0/\lambda)^2]^{-1}.$$

Here, S_0 is an average oscillator strength, and λ_0 is an average oscillator position. From the experimental results as shown in Fig. 2, the values of $S_0=0.82\sim0.88\times10^{14}\ \mathrm{m}^{-2}$ and $\lambda_0=0.226\sim0.238\ \mu$m were obtained for the single crystalline PLZT film on sapphire. The values of S_0 and λ_0 for the films on $SrTiO_3$ and spinel were very close to the above values. The dispersion parameter $hc/(e\lambda_0S_0)$ obtained from the above results takes the value of $6.23\sim6.35\times10^{-14}\ \mathrm{eVm}^2$. Following the model proposed by Didomenico *et al.*, the value takes $(6\pm0.6)\times10^{-14}\ \mathrm{eVm}^2$ in perovskite structures.[11] And, in a perovskite structure including Pb atoms at

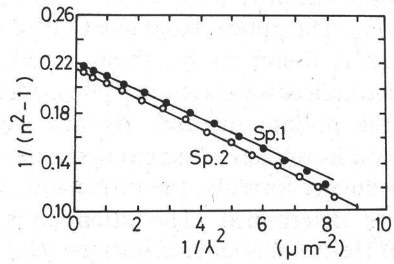

Fig. 2. Sellmeier relation for PLTZ films on sapphire. Sp. 1: prepared at 700°C, and Sp. 2: prepared at 750°C.

A sites, the value becomes smaller owing to the contribution of Pb^{2+} ions to electronic polarization.[11] However, the value for single crystalline PLZT in this study is in considerable agreement with those for single crystals of $BaTiO_3$ and $SrTiO_3$. The value is almost the same as that of PZT (65/35) ceramics,[12] but fairly larger than the reported values for PLZT (10/65/35) ceramics.[13]

§4. Application

Since the refractive index of the substrate is selected to be lower than that of PLZT, light can be guided into the PLZT thin film light waveguide. Guiding characteristics of He-Ne laser light were studied using a rutile prism (refractive index $n_e = 2.872$). Attenuation of the guided light was measured by detecting the scattered light from the surface of the PLZT light waveguide with an optical fiber and a photomultiplier. In Fig. 3, the intensity of the scattered light against the distance from the guided point is shown for TE_3-mode guided light in the PLZT film (thickness of 1.06 μm) on sapphire. The attenuation constant of 10 db/cm is obtained from the slope of the curve. Since the film thickness is rather thick and light of other mode is thought to be also guided, the value may stand for the attenuation constant for multi mode light. The value can be improved for single mode guiding in a thinner film. Since the PLZT film has rather large electrooptic effect,[6,7] the film can be used as a guide type light modulating device which operates with very low applied voltage compared with that made of $LiNbO_3$.[14]

§5. Conclusion

Using rf-sputtering at relatively low temperature, single crystalline PLZT thin films were obtained on single crystals of sapphire, $SrTiO_3$ and spinel. Crystallinity studied by X-ray diffraction was proved to be better for the film on $SrTiO_3$. The optical band gap of PLZT thus prepared is found to be about 2.8 eV. The refractive indices were accurately determined by using the m-lines method. By the study of dispersion in refractive indices using the single term Sellmeier formula, the dispersion parameter was determined. The attenuation constant of He-Ne light guided into the PLZT film was obtained. Possibility of utilization of the epitaxial single crystals of PLZT was proposed.

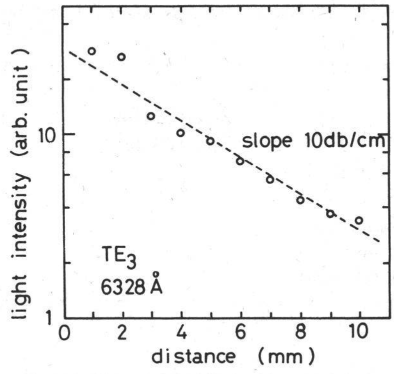

Fig. 3. Attenuation of guided light.

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