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IMPROVEMENT OF THE PHOTOVOLTAIC CURRENT FOR THE NON-BIAS OPTICAL SENSOR IN A LAYERED FILM STRUCTURE

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ABSTRACT

Photovoltaic (Pb,La)(Zr,Ti)O_3 (PLZT) films in a layered structure of different crystallographic orientations are fabricated by an optimized metalorganic deposition (MOD) method. Such films of (001) orientation exhibit a photovoltaic electrical power of approximately 20 times higher than that of random films. The anisotropic optical properties of the oriented films, including dark conductivity, photoconductivity and photovoltaic tensor surfaces, are obtained quantitatively. These results show that the photovoltaic output current and power of the oriented films are highly improved to be equal to those of semiconductors and suitable for application in the optical sensor of micro-electro-mechanical systems (MEMS).

1. INTRODUCTION

There are several types of ferroelectric material that exhibit photovoltaic effects under near-ultraviolet illumination.[1]-[4] The behavior of the photovoltaic effect of ferroelectrics is similar to but entirely different from that of semiconductor p-n junctions. It is not necessary for the photovoltaic effect of the ferroelectrics to apply the bias voltage into its interface in order to extract the electrical output, while it is necessary for the semiconductor p-n junction. Therefore, the photovoltaic effect of ferroelectrics is a simple mechanism of the current source of optical sensors that are promising in micro-electro-mechanical systems (MEMS).[5]-[7]

There are three types of photovoltaic samples[8], namely, a bulk single plate[9], a bulk bimorph[10] and a film[11]. The single plate[9] exhibits a high voltage. The bimorph[10] has a large degree of distortion and a fast mechanical response, and is suitable for mechatronics. The film[11] shows a high current output and is a good current source of the optical sensor of the MEMS. Our structural design including a modified electrode configuration, called the "layered film structure", was introduced into a PLZT film. The layered film was proved to be useful mainly due to the following properties[8]:(1)simple characteristic mechanisms,(2) a high output current of more than 1 μA, (3)easily controllable parameters, (4)a high reduction in poling voltage and (5)an improved response.

The photovoltaic effect of the ferroelectrics has an advantage in nonbias mechanisms, as mentioned above, but the output current of the ferroelectrics is almost the same as that of the semiconductors. Futher improvement of the output current, for example, by more than 10 times, could be effective in the establishment of the property of the ferroelectrics over the semiconductors. Recently, several microstructures and/or microtextures, such as a microscopic defect[12]-[15], a crystallographic orientation[16][17] and a domain structure[18] have been reported to play an essential role in the characterization of the ferroelectrics. The characteristics of the random PLZT film used in our previous study[11] are generally assumed to be inferior to those of an oriented PZT film[17][19]. Therefore, objectives of this study are to clarify the possibility of improving of the ferroelectric photovoltaic effect by controlling the microstructures and/or microtextures, i.e. (1) to establish an approximate method of preparing layered orientated crystalline films, (2) to measure the photovoltaic effect of the layered oriented films and (3) to clarify the possibility of improving the photovoltaic output of the oriented films. As a result, films of (001) preferential orientation with a

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photovoltaic electrical power output of 20 times higher than that of previously reported films of random orientation were formed. The details of preparation and experimental results are shown as follows.

2. EXPERIMENT

Among several kinds of photovoltaic material, we chose lead lanthanum zirconate titanate as the first material in our study. Lead lanthanum zirconate titanate, i.e., $Pb_{1-x}La_x(Zr_yTi_z)_{1-x/4}O_3$ (abbreviated PLZT or PLZT(X/Y/Z), where X = 100x, Y = 100y and Z = 100z), is a ferroelectric solid solution with a wide range of material properties that are dependent on its composition [20]. A PLZT film was prepared by a previously reported MOD method[11]. The crystallographic orientation depends on the prolysized temperature of a precursor[19][21]-[24]. Thus, heat treatment was performed in a rapid thermal annealing (RTA) furnace as follows: drying at 120°C for 2 min, then the formation of the precursor at 250°C for 5 min ((001) orientation) or 450°C for 5 min ((111) orientation), and finally, crystallization at 650°C for 2 min. This is almost the same as the procedure reported previously in the sol-gel method[19][25]. Standard methods were used to estimate the characteristics of the film: scanning electron microscopy (SEM) and X-ray diffraction (XRD) and photovoltaic effect analyses. Optical measurements were carried out using a previously reported system[10][11][26].

3. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD profiles of layered oriented films. Figure 1(a) shows the XRD profile of the layered oriented film of (001) preferential orientation, and Fig.1(b), that of the layered oriented film of (111) preferential orientation. The presence of a typical perovskite structure was confirmed. The thickness of the formed films was determined to be approximately 2 μm by SEM observation. Figures 2 shows the photovoltaic properties of the (001)-oriented film; the lines indicate different light intensities. The photovoltaic current was linear with respect to the induced voltage. This photovoltaic behavior was considered to result from the same mechanisms exhibited by bulk PLZT[27]. The photovoltaic voltage and current reached 1.1 V and 1.0 μA, respectively, at the highest illumination intensity region of 60 mW/cm^2.

Table I shows the observed experimental results of the photovoltaic properties of the oriented and random films. The photovoltaic current is defined as the output current in the case of zero applied voltage. Table II shows the calculated photovoltaic effect for comparison. The differences in illuminated area and light intensity

Table I Experimental conditions

• Raw material	PLZT(3/52/48) MOD solution
• Pb additional	7wt%
• Density	20wt%
• Substrate	Pt/Ti/SiO_2/Si SiO_2:thermal oxidation Pt/Ti:sputering
• spin coat	500rpm 3s 4000rpm 20s
• heat treatment	120℃ 2min., 250℃(001), 400℃(111) 5min., 650℃ 2min. RTA-furnance
• upper electrode	ITO sputtering

were calculated using the same volume unit, such as the illumination area of 10 x 10 mm^2 of illumination area, the thickness of 4 μm and the light intensity of 150 mW/cm^2. The illuminated light will reach at 100μm in depth that has already been reported previously[28]. This means that the output of photovoltaic effect in a unit volume of layered film that thickness is at most few micro meters. The film of (001) preferential orientation film show an electrical power output 20 times higher than that of the films of random orientation. The films of (111) preferential orientation shows the electrical power output 7 times higher than that of the films of random orientation. These results confirm that the output of the photovoltaic effect of the films of crystallographic orientationis superior to that of the films of random orientation.

The current density j_i is expressed in terms of the applied electric field E and the light intensity J. $\vec{e}$ is the

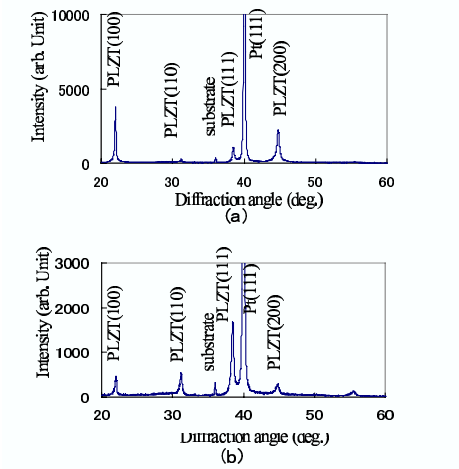

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Fig.1 XRD profiles of (a)(001) and (b)(111) oriented film.

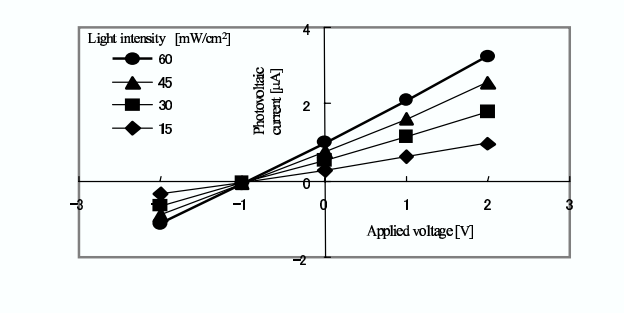

Fig.2 Photovoltaic current with respect to applied voltage at four kinds of light intensity.

Table I. Directly observed photovoltaic currents of oriented and random films. In the oriented film, the thickness, illumination area and light intensity are 2 μm, 2 x 14 mm^2 and 60 mW/cm^2, respectively. In the random film, these are 4μm, 10 x 10 mm^2 and 150 mW/cm^2, respectively.

Sample	Photovoltaic current [μA]	Photovoltaic voltage [V]	Reference
			$j_{[111]} = 0.$
PLZT(001) oriented	1.07	0.96	This work
PLZT(111) oriented	0.43	0.82	This work
PLZT random	1.70	0.85	11

Table II Comparison of the output current and electrical power of oriented and random films. The output is calculated under the same conditions for comparison; the area is 10 x 10 mm^2, the thickness is 1 μm and the light intensity is 150 mW/cm^2.

Sample	Photovoltaic current [μA]	Electrical power [μW]	Reference
PLZT(001) oriented	19.1	55.0	This work
PLZT(111) oriented	7.7	19.1	This work
PLZT random	1.7	2.9	11
PLZT bulk	2 x 10^{-4}	0.16	12

polarization unit vector of incident light[2].

$$j_i = \sigma_{ij}^d E_j + \sigma_{ij}^{ph} E_j J + \beta_{ijl} e_j e_l^* J \qquad (1)$$

Here, σ_{ij}^d is the dark conductivity, σ_{ij}^{ph} photoconductivity and β_{ijl} the photovoltaic coefficient. Summation is understood using the identical subscripts here. The last term describes the photovoltaic effect, namely, the light generating a direct current in the absence of external fields. The dark conductivity σ_{ij}^d, photoconductivity σ_{ij}^{ph} and photovoltaic coefficient β_{ijl}, are calculated quantitatively from eq.(2), Fig.2 and the symmetry of the material. The poled and oriented film with a $C_{\infty v}$ symmetry has five non-zero linear photovoltaic tensor components[28][29], namely, $\beta_{31}, \beta_{32}(=\beta_{31})$, β_{33}, β_{15} and $\beta_{24}(=\beta_{15})$. Using this definition and tensor expressions, j_i is expressed as

$$j_{[001]} = \beta_{31} J, \qquad (2)$$

$$j_{[111]} = 0.2\beta_{33}J + 0.4\beta_{31}J + 0.8\beta_{15}J \cong 0.2\beta_{33}J + 0.4\beta_{31}J \qquad (3)$$

The results obtained are shown in Table III. β_{15} is much smaller than β_{31} and β_{33}, and is considered zero[2]. The photon momentum, nonlinear effect, photoentrainment and polarization effects are omitted in this consideration, which is good within the precision of the experiment. The coefficients of the (001) orientation are larger than those of the (111) and random orientations. Photoconductivity is high in a current density range of more than over 10 mW/cm^2. Dark conductivity and photoconductivity have been reported in the case of bulk but not the photovoltaic coefficient. The photovoltaic coefficient of PLZT is smaller than that of single crystals except $Pb_5Ge_3O_{11}$. On the other hand, the photoconductivity of PLZT is larger than that of single crystals. The observed current of PLZT is more than 1 μV due to this large photoconductivity.

The optical properties of polycrystalline materials, for example, ferroelectric ceramics[2] and polymers[32][33], have been reported to show the general tensor description. The tensors of polycrystalline materials, for example, a gyration tensor[31][32], have also been reported but not photovoltaic tensors. Figure 3 shows the cross section of the tensor surface[34][35] cut in the yz(010) plane, where the distance from the origin to the surface corresponds to the magnitude of the photovoltaic effect. The anisotropic

properties of the photovoltaic effect in a layered film structure have not yet been reported. The tensor surface is

Table III Dark conductivity, photoconductivity and photovoltaic coefficients of PLZT films and bulk, and other materials. The dashed line indicates that there is no report on the point in the corresponding references

Sample	Dark conductivity $10^{-9}[\Omega^{-1}m^{-1}]$	Photo-conductivity $10^{-11}[\Omega^{-1}mW^{-1}]$	Photovoltaic coefficient $10^{-11}[V^{-1}]$	Wavelength of incident light [nm]	Reference
PLZT(001) oriented	6.2	12	13	365	This work
PLZT(111) oriented	2.6	5.2	5.4	365	This work
PLZT random	1.6	2.8	2.8	365	11
PLZT bulk	2.7×10^{-2}	0.2	------	365	27
$LiNbO_3$+Fe0.003wt %	———	4.5×10^{-4}	5.0×10^{2}	440	2
$Bi_{12}SiO_{20}$	———	———	6.0×10^{2}	488	2
$KNbO_3$+Fe0.065wt%	7.0×10^{-3}	9.3×10^{-3}	1.2×10^{2}	488	2
$Pb_5Ge_3O_{11}$	1.7	———	9.0	440	2

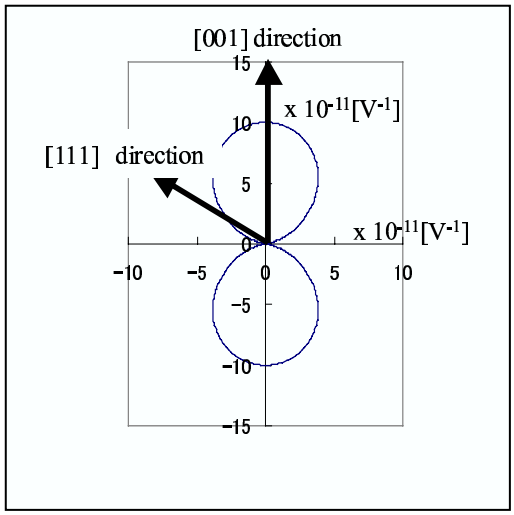

Fig.3 Cross-sectional figure of the photovoltaic tensor surface.

expected to reproduce the optical anisotropy very well. This result indicates that the (001) direction shows the highest photovoltaic effect. The entire surface has an ∞ rotational symmetry axis in the [001] direction.

There has been a report on the relationships between the crystallographic orientation and certain physical properties[18][22]-[25]. In a PZT system, there could be two kinds of crystalline orientation, namely, (001) and (111). The (001) orientation shows better dielectric and piezoelectric properties than the (111) orientation. On the other hand, the (111) orientaion shows better ferroelectric properties such as a coercive field and remanent polarization[18][22] than the of (001) orientation. This report also indicates that the dark conductivity, photoconductivity and photovoltaic coefficient of the (001) orientation are higher than those of the (111) orientation. Thus, it is suggested that the photovoltaic effect is more closely related to the electrical properties than to the ferroelectric properties. The outputs of the bulk and film of random orientation were previously confirmed to be almost the same qualitatively and quantitatively[12]. In addition to this, photoconductivity was determined to play an important role in photovoltaic effect.

4. CONCLUSIONS

The conclusions of this article are summarized as follows: (1) Films of (001) and (111) preferrential orientations wer prepared by the MOD method by controlling the heating treatment of the precursor. (2) Films of (001) orientation exhibited a photovoltaic electrical power 20 times higher than that of films of random orientatation[11]. (3) The dark conductivity, photoconductivity and photovoltaic coefficient of the oriented films were determined. The tensor surface showing the photovoltaic effect was also determined. (4) The control of the orientation was effective for the photovoltaic effect and suitable for the current source of the optical sensors of micro-electro-mechanical systems (MEMS). The oriented films showed a higher electrical power than the random films.

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6. REFERENCES

[1] V.M. Fridkin, *Photoferroelectrics,* (Springer-Verlag, New York, 1979).
[2] B.I. Stuman and V.M. Fridkin, *The photovoltaic and photorefractive effects in noncentrosymmetric materials*, (Gordon and Breach Science Publishers, U.K., 1992).
[3] A.M. Glass, D. von der Linde and T.J. Negran, *"High-voltage bulk photovoltaic effect and the refractive process in $LiNbO_3$",* Appl.Phys.Lett. vol.25, pp. 233-235, 1974.
[4] G. Dalba, Y. Soldo, F. Rocca, V.M. Fridkin and Ph. Sainctvit, *"Giant bulk photovoltaic effect under linearly polarized X-ray synchrotron radiation", Phys.Rev.Lett.* vol.74, pp.988-991, 1995.
[5] J.J.Tsaur, Z.J.Wang, L.Zhang, M.Ichiki, J.W.Wan and R.Maeda, "*Preparation and application of lead zirconate titanate (PZT) films deposited by hybrid process: Sol-gel method and laser ablation*", Jpn.J.Appl.Phys., vol.41, pp.6664-6668, 2002.
[6] X.C.Shan, R.Maeda, T.Ikehara, H.Kanegari and T.Hattori, *"Applications of micro hot embossing for optical switch formation*" Sensors and Actuators, vol.A119, pp.433-440, Sensors and Actuators, A108, 224, (2003).
[7] R.Maeda, J.J.Tsaur, S.H.Lee and M.Ichiki, "*Piezoelectric microactuator devices*", J.Electroceramics, vol.12, pp.89-100, 2004.
[8] T.Kobayashi, M.Ichiki, H.Furue, R.Maeda, Y.Morikawa and K.Nonaka, "*Preparation and its photovoltaic effect of ferroelectric film"*, Key Engineering Materials, vol.301, pp.193-196, 2005.
[9] Y. Morikawa, M. Ichiki and T. Nakada, "*Bimorph type optical actuator using PLZT elements*", Jpn.Soc.Mech.Eng., vol.C69, pp.361-366, 2000.
[10] P.S. Brody, "*Optomechanical bimorph actuator*", Ferroelectrics vol.50, pp.27-32, 1983.
[11] M.Ichiki, R.Maeda, Y.Morikawa, Y.Mabune, T.Nakada and K.Nonaka, "*Photovoltaic effect of lead lanthanum zirconate titanate in a layered film structure design*", Appl.Phys.Lett., vol.84, pp.395-397, 2004.
[12] K. Nonaka, M. Akiyama, A. Takase, T. Baba, K. Yamamoto and H. Ito, "*Photovoltaic response map in PLZT ceramics depoed with various impurity elements*", J.Mat.Sci.Lett., vol.15, 2096-2098, 1996.
[13] X.Ren, "*Large electric-field-induced strain in ferroelectric crystals by point-defect-mediated reversible domain switching*", Nature Materials, vol.3, pp.91-94 , 2004.
[14] M.Venkatesam, C.B.Fitzgerald and J.M.D.Coey, "*Thin films: Unexpected magnetism in a dielectric oxode*", *Nature*, vol.430, p.630(2004).
[15] K. Nonaka, M. Akiyama, T. Hagio and A. Takase, "*Effect of Pb/(Zr + Ti) molar ratio on the photovoltaic properties of lead zirconate titanate ceramics*", *J.Eur.Ceram.Soc.* vol.19, pp.1143-1148, 1999.
[16] R.Ramesh and D.G.Schlom, "*Orienting Ferroelectric films*", Science, vol.296, pp.1975-1976, 2002.
[17] H.Matsuda, S.Ito and T.Iijima, "*Uniform field-induced strain in a/b-axes oriented $Bi_{3.9}Pr_{0.1}Ti_3O_{12}$ thick film on IrO2/Si substrate for lead free piezoelectric microdevice applications*", Appl.Phys.Lett., vol.85, pp.1220-1222, 2004.
[18] S.Wada, H.Yasuno, T.Hoshina, S.M.Nam, H.Kakemoto and T.Tsurumi, "*Preparation of nm-sized bariumu titanate fine particle and their powder dielectric properties*", Jpn.J.Appl.Phys., vol.**42**, pp.6188-6195, 2003.
[19] Z.J. Wang, I. Karibe, R. Maeda and H. Kokawa, "*Preparation of lead zirconate titanate thin films derived by hybrid processing : Sol-gel and laser ablation*", J.Am.Ceram.Soc., vol. 85, pp.3108-3110, 2002.
[20] G.H. Haertling and C.E. Land, "*Hot-pressed $(Pb,La)(Zr,Ti)O_3$ ferroelectric ceramics for electrooptic applications*", J.Am.Ceram.Soc. vol.54, pp.1-11, 1971.
[21] T.Kobayashi, M.Ichiki, J.J.Tsaur, and R.Maeda, "*Effect of multi-coating process on the orientation and microstructure of lead zirconate titanate (PZT) thin films derived by chemical solution deposition*", Thin Solid Films, vol.489, pp.74-78, 2005.
[22] A.Wu, P.M.Vilarinho, I.M.M.Salvado, J.L.Bastista, Z.Zhou, I.R.Reaney, A.R.Ramos and M.F.da Silva, "*Effect of lead zirconate titanate seeds on PtxPb formation during the pyrolysis of lead zirconate titanate thin films*", J.Am.Ceram.Soc., vol.85, pp.641-646, (2002).
[23] S.Y.Chen and I.W.Chen, *J.Am.Ceram.Soc.*, "*Texture development, microstructure evolution , and crystallization of chemically derived PZT thin films*", J.Am.Ceram.Soc., vol.81, pp.97-105, 1998.
[24] Z.J.Wang, H.Kokawa, R.Maeda and M.Ichiki, "*Electrical properties and microstructure of lead zirconate titanate thin film in situ grown hybrid processing: Sol-gel method*

and pulsed laser deposition", Jpn.J.Appl.Phys., vol.43, pp.6554-657, 2004.
[25] Z.J. Wang, K. Kikuchi and R. Maeda, "*Effect of Pb content in target on electrical properties of laser ablation derived lead zirconate titanate thin film*", Jpn.J.Appl.Phys. vol.39, pp.5413-5417, 2000.
[26] K. Kawaguchi, M. Ichiki, Y. Morikawa and T. Nakada, "*Electrical properties of PLZT and its application to optical motor*", Ferroelectrics vol.273, pp.41-46, 2002.
[27] K. Nonaka, M. Akiyama, T. Hagio and A. Takase, "Bulk photovoltaic effect in reduced/oxidized lead lanthanum zirconate titanate ceramics", *Jpn.J.Appl.Phys. vol.34, pp.2344-2349, 1995.*
[28] T.Nakada, D.H.Cao, Y.Morikawa, M.Kimura and C.Y.Hsien, *"Study on optical servo system ",* J.Soc.Mech.Eng. vol.59,pp.206-212, 1993.
[29] W.G.Cady, *Piezoelectricity*, (Dover Publications Inc., New York, 1964).
[30]I.S.Zheldev, *Symmetry and its application*, (Kodansya, Tokyo, 1979, translated into Japanese by Y.Ishibashi and M.Nakayama).
[31] J.Kobayashi, T.Asahi, M.Ichiki, K.Saito, T.Shimasaki, H.Yoshii, Y.Itagaki and H.Ikawa, "*Optical study on the phase transition of lead lanthanum zirconate titanate* $Pb_{0.92}La_{0.08}(Zr_{0.70}Ti_{0.30})_{0.98}O_3$ *ceramics*", Phys.Rev., vol.B51, pp.763-778, 1995.
[32] J.Kobayashi, T.Asahi, M.Ichiki, A.Oikawa, H.Suzuki, T.Watanabe, E.Fukada and Y.Shikinami*,"*Structural and optical properties of poly lactic acids*", J.Appl.Phys., 77, 2957 (1995).*
[33] T.Furukawa, *"Structure and functional properties of ferroelectric polymers", Advances in. Colloid and Interfaces Sci., vol.71-72, pp.183-208, 1997.*
[34] A.V.Shubnikov*, Principles of optical crystallography* (Consultants bureau, New York, 1960).

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