Sensors and Materials, Vol. 16, No. 4 (2004) 181–189
MYU Tokyo

S & M 0556

Formation and Characteristics of Photovoltaic PLZT Ceramics in Layered Film

Masaaki Ichiki, Yasushi Morikawa[1], Yosuke Mabune[2], Takeshi Nakada[2], Kazuhiro Nonaka[3] and Ryutaro Maeda

Institute of Mechanical System Engineering, National Institute of Advanced Industrial Science and Technology, 1-2 Namiki, Tsukuba, Ibaraki 305-8564, Japan
[1]Intelligent System Institute, National Institute of Advanced Industrial Science and Technology, 1-2 Namiki, Tsukuba, Ibaraki 305-8564, Japan
[2]School of Information Environment, Tokyo Denki University, 2-1200 Muzai-Gakuendai, Inzai, Chiba 270-1382, Japan
[3]Institute for Structural and Engineering Materials, National Institute of Advanced Industrial Science and Technology, 807-1 Shuku-machi, Tosu, Saga 841-0052, Japan

(Received March 2, 2004; accepted July 21, 2004)

Key words: photovoltaic effect, PLZT, layered film, perovskite structure, transducers, MEMS

This paper reports on the formation of a layered film and the highly improved photovoltaic output of the lead lanthanum zirconate titanate (PLZT) layer employed. The structural design is described using a top transparent indium tin oxide (ITO) electrode. The PLZT film exhibited V and μA output induced by light irradiation. The photovoltaic current of the PLZT film was more than 10^2 times larger than that of bulk PLZT, while the photovoltaic voltage per unit thickness in the layered film was almost the same as that in bulk ceramics and single crystals. These differences are due to the characteristics of the film and the configuration of the electrode. The PLZT film also has the advantage of easily controllable parameters: film thickness, illuminated area and illumination intensity. A simple model is used for the phenomenological explanation of the improved photovoltaic effect of the PLZT film.

*Corresponding author, e-mail address: ichiki-m@aist.go.jp

1. Introduction

Several kinds of ferroelectric materials exhibit the photovoltaic effect under near-ultraviolet illumination,[1–3] as shown in Fig. 1. The most outstanding advantage of the photovoltaic effect is its high output voltage of over 1 kV. This behavior of ferroelectrics is entirely different from that of the semiconductor p-n junction, because the photovoltaic effect occurs within the material and is considered to be an optical property of the material itself. On the other hand, the semiconductor p-n junction is a property of the interface and not of a material. The photovoltaic effect has promise for application in the following areas: 1) high electrical output voltage over 1 kV, 2) functioning as a transducer for converting optical energy into electrical energy, and 3) wireless energy transfer. These characteristics are useful and applicable to micro-electromechanical systems (MEMS).[4–6]

Among such photovoltaic materials, lead lanthanum zirconate titanate is the most popular. Lead lanthanum zirconate titanate, i.e., $Pb_{1-x}La_x(Zr_yTi_z)_{1-x/4}O_3$ (abbreviated to PLZT or PLZT(X/Y/Z), where X = 100x, Y = 100y and Z = 100z), is a ferroelectric solid solution with wide-ranging material properties that depend on its composition.[7] PLZT was first developed as a ferroelectric transparent ceramic. PLZT(3/52/48) has photostrictive properties as a result of the superposition of photovoltaic and inverse piezoelectric effects. The photostrictive effect is induced by illuminating the material in the near-ultraviolet region. Some devices or systems that make use of photovoltaic materials are under development, and they are mainly divided into two categories: devices which use the photostrictive effect, and devices which use the photovoltaic effect[8–10] and its related electrostatic force.[11,12] Some reports have been published from the point of view of the material aspect; *e.g.,* the impurity doping effect,[13] the firing atmosphere effect,[14] and the molar ratio dependence.[15] However, there have been very few works carried out seeking to clarify the mechanisms of the photovoltaic effect. Glass *et al.* explained that the photovoltaic effect was due to the nonequivalent excitation of electrons from the impurity

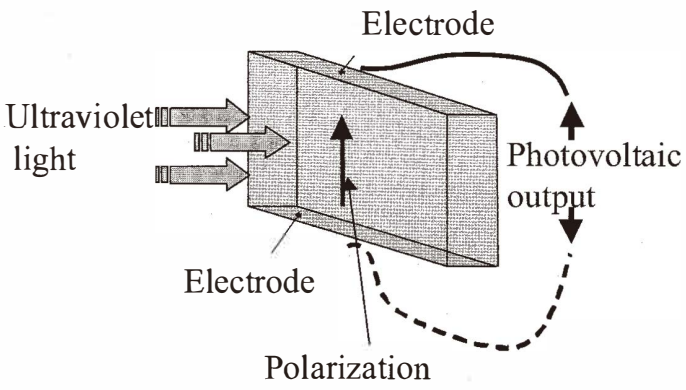

Fig. 1. Representation of photovoltaic effect of PLZT.

level to the conduction band.[16] There is, however, no universal interpretation of the ferroelectric photovoltaic effect. Such reported results are only applicable to a limited number of materials and observations.

Little has been, so far, reported on the improvement of the photovoltaic effect, and the improvements realized were within one order of magnitude of previous results.[13-15] Other problems have not yet been fully overcome, such as the slow response of the photostrictive effect in the range of the second order due to the high electrical resistance of PLZT. In fact, the response of the photovoltaic current should be reasonably fast considering the electrical equivalent model.[17] It would be therefore useful to build in the improved output of the photovoltaic current to achieve fast-response devices. Only bulk ceramics and single crystals have been used as photovoltaic materials, but illuminated light is absorbed in a very thin region of the surface layer about 100 μm thick in these materials.[18] The photovoltaic effect thus occurs in only a limited region of the total volume of these materials. The nonilluminated parts of these materials do not act as electrical sources of the photovoltaic effect. For this reason a film is more useful than bulk material in terms of photovoltaic effect efficiency. A film structure is, however, not suitable for MEMS if the pure miniaturization of bulk materials is achieved. Our new structure design, including a modified electrode configuration, was introduced into a layered PLZT film.

Recently, we fabricated PLZT films on a trial basis and confirmed that the efficiency of the films was better than that of bulk material. We describe the sample preparation and its characteristics in the following sections. We also present a phenomenological explanation of the improved photovoltaic effect attainable with PLZT films.

2. Preparation of PLZT Film

It is necessary to sandwich the ferroelectric film between two electrodes for its characteristics to appear. There are two possible locations for the electrodes on the film. One sites the electrodes on either side of the film and the other has the electrodes on the upper and lower surfaces of the film. We chose the latter style for this experiment because it is suitable for the MEMS fabrication process and it decreases the poling voltage significantly. Figure 2 is a cross-sectional illustration of the structure of the PLZT film. However, since it was necessary to illuminate through the upper electrode, a transparent upper electrode was used.

The PLZT film was formed using metal organic deposition (MOD) on a Si-substrate, with the lower electrode sputtered onto the substrate. Then, the photovoltaic effect was estimated. The Si-substrate was prepared using the standard MEMS process in our group.[4-6] The PLZT film was formed on the prepared Pt/Ti/SiO_2/Si substrate. The raw solution of PLZT was a commercially available MOD solution. The composition of PLZT was (3/52/48), and the excess Pb ratio was 7% with respect to its quantitative chemical composition. The PLZT content of the solution was 20 wt%. The substrate was dipped into the liquid solution and rotated with a spin coater. Heat treatment was carried out in a furnace as follows: drying at 120°C for 10 min, then formation of precursor at 470°C for 30 min and finally crystallization at 600°C for 30 min. This is almost the same as the

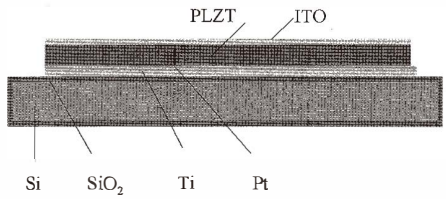

Fig. 2. Cross-sectional view of layered PLZT film.

procedure used in the sol-gel method.[19] These steps were repeated 10 times to form the film. Indium tin oxide (ITO) was sputtered to fabricate the upper electrode to enable the estimation of the photovoltaic effect and the dielectric and ferroelectric properties of the film.

Standard methods were used to estimate the material characteristics: scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, measurement of the dielectric constant and photovoltaic effect. Photovoltaic current was estimated using an electrometer (Keithley 6517). Photovoltaic voltage was estimated indirectly using the bias induction function of the electrometer. Details on the use of this method have been reported previously.[20]

3. Experimental Results and Discussion

Figure 3(a) shows an SEM image of the surface and Fig. 3(b) a cross- sectional image of the formed film. The acceleration voltage of the SEM was 8 kV. The thickness of the film was 4 μm. The lower gray part of the PLZT film is SiO_2. The SEM inspection confirmed that the film was homogeneous. The interface between the lower electrode and the PLZT film was flat and smooth without voids or deficiencies. Figure 4 shows an XRD profile of the PLZT film. The X-ray power was 40 kV and 30 mA. The presence of a typical perovskite structure was confirmed. No particular crystal orientation was observed and a random orientation was confirmed. The film had no pyrochlore or amorphous structure. Table 1 shows the representative material characteristics of the PLZT film including its dielectric constant. We note that the dielectric constant (1100) of the PLZT film was almost the same as that of bulk PLZT (1000~1200), so the quality of the film is adequate in terms of electrical properties. Figures 5(a) and 5(b) show the photovoltaic current and voltage, respectively. The photovoltaic current was linear with illumination intensity. The photovoltaic voltage saturated to a constant value as illumination intensity increased. This photovoltaic behavior is caused by the same mechanisms exhibited by bulk PLZT.[14] The photovoltaic voltage and current reached 0.9 V and 1.7 μA in the region of highest illumination intensity at 150 mW/cm^2. The light source was a Hg lamp with a wavelength filter. The filtered light had its maximum intensity at a wavelength of 365 nm. The output level of the photovoltaic current of the PLZT film was twofold higher than that of bulk PLZT.[21] On the other hand, the photovoltaic voltage of the PLZT film was threefold lower than that of bulk PLZT.[21] Table 2 compares PLZT in film and bulk

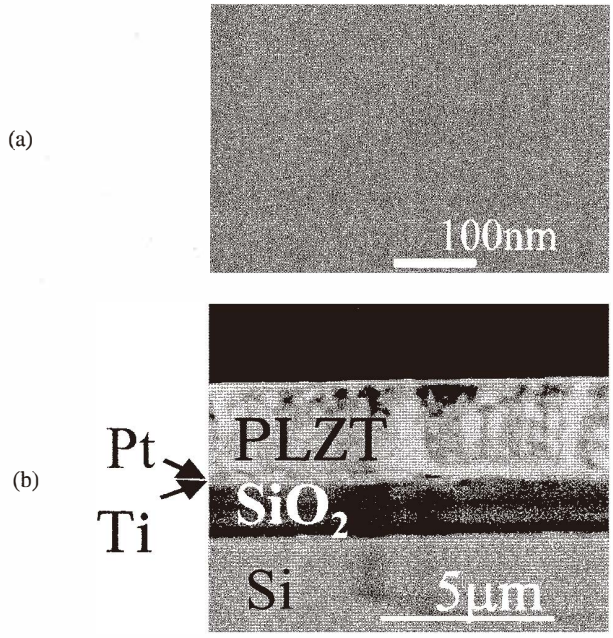

Fig. 3. SEM figure of (a) surface and (b) cross section of PLZT film.

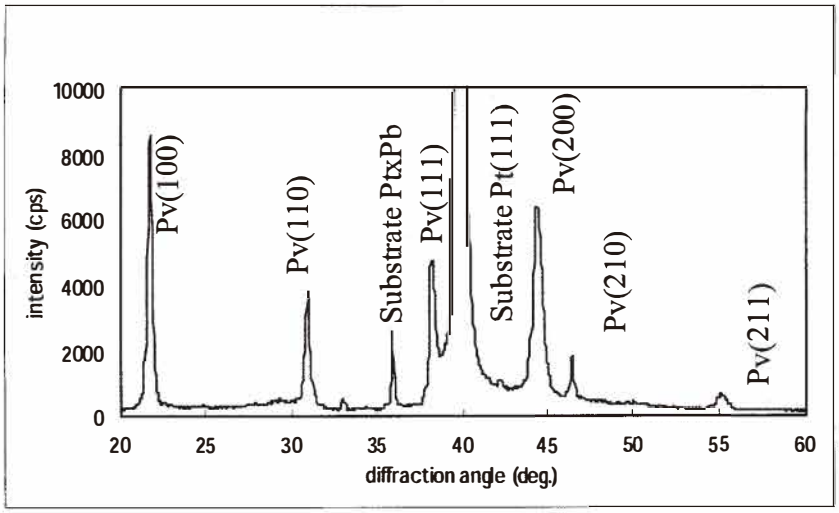

Fig. 4. X-ray diffraction profile of PLZT film.

Table 1
Summary of material preparation and characteristics.

Composition	PLZT(107/3/52/48) + 7 w%Pb (available in market)
Substrate	$Pt/Ti/SiO_2/Si$
Thickness of film	4 μm
Area	10×10 (mm^2)
Number of coating repetitions	10 repetitions
Upper electrode	ITO (sputtered)
Dielectric constant	1100
Crystal structure	Perovskite
Crystal orientation	Random

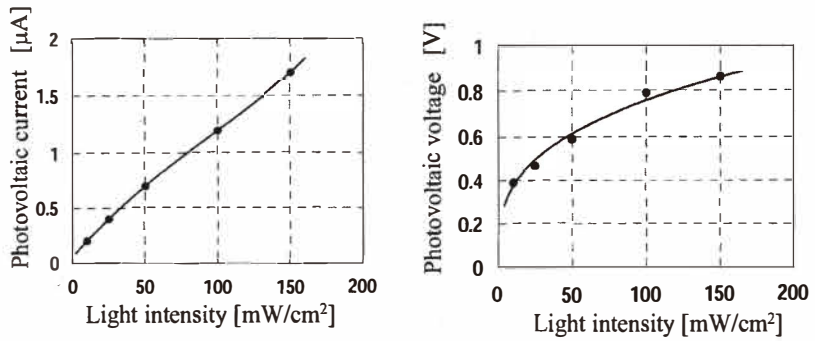

Fig. 5. Photovoltaic effect of layered PLZT film. Relationships between (a) photovoltaic current and (b) photovoltaic voltage and illumination intensity.

Table 2
Comparison of the photovoltaic properties of PLZT in bulk and layered film forms.

	Bulk ceramics	Layered film
Sample size w × h × t (mm)	$10.2 \times 5.1 \times 2.4$	$10.0 \times 10.0 \times 0.004$
Polarization direction	height	height
Illumination direction	width	height
Illumination volume (mm^3)	$10.2 \times 5.1 \times 0.1$	$10.0 \times 10.0 \times 0.004$
Photovoltaic current (nA)	16.8	1700
Photovolaic voltage (V)	2067	0.9
Photovolaic current density (nA/cm^2)	70	1700
Photovoltaic electric fild (kV/cm)	4053	2250

forms.[21] The output current and voltage per unit are almost the same in both film and bulk PLZT. Light can be illuminated into the entire volume of the layered film. However, illuminated light was absorbed within the surface of 100 μm thickness. The photovoltaic current of bulk PLZT can go through a limited area (10.2 mm × 0.1 mm).

Because bulk PLZT exhibits a high photovoltaic voltage of over 1 kV and a small photovoltaic current of around 10 nA per square centimeter of area (h × t) and millimeter of width (w), it is difficult to explore useful and practical applications with this output level. These differences are due to the characteristics and also the configuration of the electrode. We present a phenomenological explanation of the improved photovoltaic effect using a simple model. Figure 6 shows bulk ceramic in (a), a layered film in (b), and film elements in (c). The width of the film elements Δw is assumed to be 10 μm. Therefore, the real film is completely connected with these film elements on the order of 10^3 times. As a result, the photovoltaic current of the film is 10^3 times that of a film element. It is assumed that the film element is illuminated from the side in (c), although the sample is actually illuminated

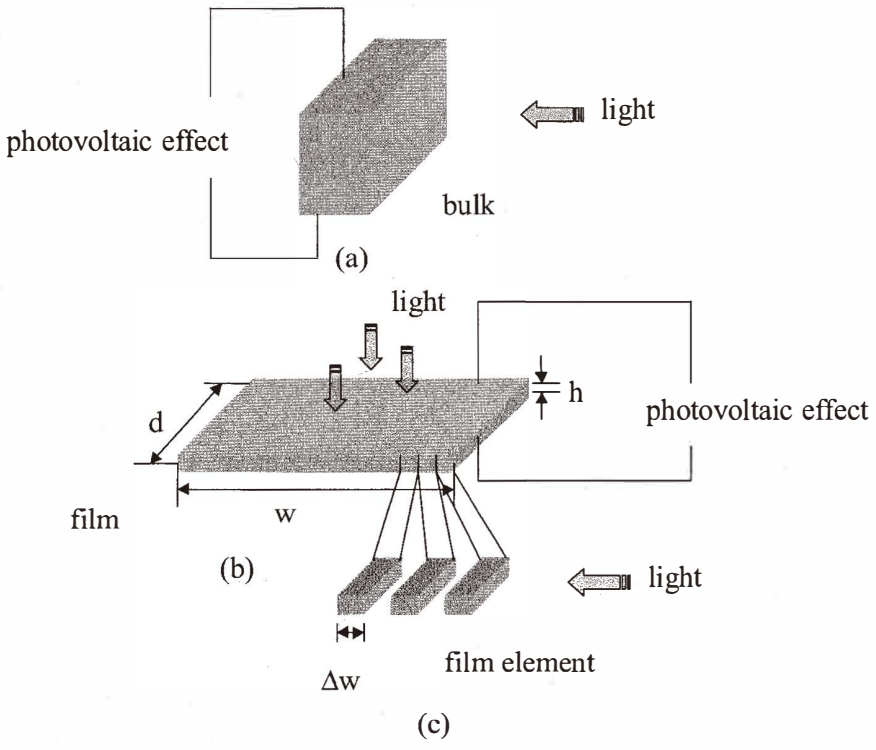

Fig. 6. Representative figure of illumination onto (a) bulk, (b) film and (c) film elements of photovoltaic materials.

from the top in (b). This assumption is valid in cases where the width Δw and thickness t of the thin film element are under 10 μm, because homogeneous illumination is achieved within such a scale. Because it is difficult to form films over 10 μm in thickness using current technology, this assumption is valid from a practical point of view. A layered PLZT film that exhibits V and μA output is more useful than conventional single crystal or bulk ceramic materials that exhibit kV and μA output. It is generally considered that the material properties of a film are lower than those of the corresponding bulk or single crystals. This was not the case in the results of our experiments as reported in this paper and shown in Table 2, because the layered film in our experiment had an electrode distance 10^{-4} times shorter than that reported in previous experiments. The electrode distance of our film was only a few micrometers, as opposed to an electrode distance of several millimeters in bulk or single crystals seen in normal and conventional use.[8–18] A film is more easily poled than bulk because of its thinness. A homogeneous material is easily and constantly achieved at a short electrode distance. This is also another advantage; it is possible to fabricate the film in an only standard technology. A homogeneously poled film leads to improved characteristics. The photovoltaic voltage is linear with electrode distance, i.e., the thickness of the film, when it is illuminated homogeneously. On the other hand, because photovoltaic current only occurs from illuminated film, the current is proportional to the illuminated area of the film. This is one of the most outstanding advantages of using a film rather than bulk ceramics or single crystals. It is necessary to illuminate the area between the electrodes when using bulk materials, but it is possible to only illuminate the necessary parts of a PLZT film. This makes it easier to control the photovoltaic output. A layered PLZT film thus has controllable parameters: film thickness, illuminated area and illumination intensity.

We have shown that a layered PLZT film has the following advantages: 1) useful level of photovoltaic V and μA output, 2) several controllable parameters to modify output characteristics, and 3) ease of film formation. In this study, we have used only standard technologies, and no particularly technical tools or processes were involved. Compared with the use of conventional photovoltaic ceramics and single crystals, the advantages are quite clear. Therefore, a layered PLZT film, as proposed in this report, is more compatible with IT electronics and MEMS.

In summary, our study has confirmed the following points. 1) A PLZT film exhibits a photovoltaic current 2 orders of magnitude higher than those exhibited by bulk ceramics and single crystals. 2) The photovoltaic current of the PLZT film is linear with the area illuminated. 3) The photovoltaic voltage per unit thickness of PLZT film is on the same order as bulk PLZT, while the photovoltaic voltage of the PLZT film is 3 orders of magnitude lower than that of bulk PLZT. 4) The improved photovoltaic effect of the PLZT film can be explained phenomenologically using a simple model.

Our next target is to control the crystal orientation,[22] heat treatment[23] and composition[24] to improve characteristics and to achieve higher photovoltaic performance. Such a layered film could be useful as an energy transducer for optical to electrical conversion and would be applicable to microscale objects rotating at fast speed (*e.g.*, ultrasonic motors) and MEMS devices.

Acknowledgments

The authors express their thanks to Ms. K. Tanaka (AIST) for the sample preparation, and Ms. T. Imai (AIST) for manuscript preparation. We are also grateful to Dr. T. Eiju and Dr. K. Tanie (AIST) for their encouragement during this study. This study was supported in part by the Grant-in-Aid for Young Scientists, 14750044 (KAKENHI) program.

The authors also show their deep appreciation to Dr. Y. Suzuki (editor of this special issue), the editorial staff of Sensors and Materials and referees for useful suggestions on technical points.

References

1 B. I. Stuman and V. M. Fridkin: The photovoltaic and photorefractive effects in noncentrosymmetric materials (Gordon and Breach Science Publishers, U.K., 1992).
2 V. M. Fridkin: Photoferroelectrics (Springer-Verlag, New York, 1979).
3 G. Dalba, Y. Soldo, F. Rocca, V. M. Fridkin and Ph. Sainctvit: Phys. Rev. Lett. **74** (1995) 988.
4 S. Matsumoto, A. Klein and R. Maeda: Proc. of IEEE Micro Electro Mechanical System. (1998) 141.
5 A. Schroth, C. Lee, S. Matsumoto and R. Maeda: Sensors and Actuators **73** (1999) 144.
6 J. Chu, Z. J. Wang, R. Maeda, K. Kataoka, T. Itoh and T. Suga: J. Vac. Sci. Tech. B **18** (2000) 3604.
7 G. H. Haertling and C. E. Land: J. Am. Ceram. Soc. **54** (1971) 1.
8 P. S. Brody: Ferroelectrics **50** (1983) 27.
9 Y. Morikawa, and T. Nakada: Jpn. Soc. Mech. Eng. Int. J. C **41** (1998) 860.
10 T. Fukuda, H. Nakamura, S. Hattori, F. Arai and H. Matsuura: Trans. Jpn. Soc. Mech. Eng. **61** (1995) 2448.
11 Y. Morikawa, M. Ichiki and T. Nakada: Jpn. Soc. Mech. Eng. C **69** (2003) 161.
12 H. Ishihara and T. Fukuda: J. Rob. Mech. **11** (1999) 436.
13 K. Nonaka, M. Akiyama, A. Takase, T. Baba, K. Yamamoto and H. Ito: J. Mat. Sci. Lett. **15** (1996) 2096.
14 K. Nonaka, M. Akiyama, T. Hagio and A. Takase: Jpn. J. Appl. Phys. **34** (1995) 2344.
15 K. Nonaka, M. Akiyama, T. Hagio and A. Takase: J. Eur. Ceram. Soc. **19** (1999) 1143.
16 A. M. Glass, D. von der Linde and T. J. Negran: Appl. Phys. Lett. **25** (1974) 233.
17 T. Nakada, D. H. Cao, M. Kimura and C. Y. Hsien: J. Soc. Mech. Eng. C **58** (1992) 189.
18 T. Nakada, D. H. Cao, Y. Morikawa, M. Kimura and C. Y. Hsien: J. Soc. Mech. Eng. C **59** (1993) 2470.
19 Z. J. Wang, K. Kikuchi and R. Maeda: Jpn. J. Appl. Phys. **38** (1999) 5342.
20 K. Kawaguchi, M. Ichiki, Y. Morikawa and T. Nakada: Ferroelectrics **273** (2002) 41.
21 M. Ichiki, Y. Morikawa and T. Nakada: Jpn. J. Appl. Phys. **11** (2002) 6993.
22 Z. J. Wang, I. Karibe, R. Maeda and H. Kokawa: J. Am. Ceram. Soc. **85** (2002) 3108.
23 M. Ichiki, L. Zhang, Z. Wang, Y. Morikawa, M. Tanaka and R. Maeda: Proc. SPIE **4467** (2001) 387.
24 J. Wang, K. Kikuchi and R. Maeda: Jpn. J. Appl. Phys. **39** (2000) 5413.