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Photovoltaic properties of lead lanthanum zirconate titanate ceramics in a layered film structure design

Masaaki Ichiki[a,*], Yasushi Morikawa[b], Takeshi Nakada[c], Ryutaro Maeda[a]

[a] *Institute of Mechanical System Engineering, National Institute of Advanced Industrial Science and Technology, 1-2 Namiki, Tsukuba, Ibaraki 305-8564, Japan*
[b] *Intelligent System Institute, National Institute of Advanced Industrial Science and Technology, 1-2 Namiki, Tsukuba, Ibaraki 305-8564, Japan*
[c] *School of Information Environment, Tokyo Denki University, 2-1200 Muzai-Gakuendai, Inzai, Chiba 270-1382, Japan*

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Abstract

This paper reports on the formation of a new layered film structure and the highly improved photovoltaic output of the lead lanthanum zirconate titanate (PLZT) employed. The new structure design is described using a top transparent indium tin oxide (ITO) electrode. The PLZT film structure exhibited V and mA output. This means that the photovoltaic current of the PLZT film per unit width was more than 10^2 times larger than that of bulk PLZT, while the photovoltaic voltage per unit thickness in the layered film structure was almost the same as that in bulk ceramics and single crystal. These differences are due to the characteristics of the film structure and configuration of the electrode. PLZT film also has the advantage of its 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.

Keywords: D. PLZT; Photovoltaic effect; Layered film structure; Perovskite structure; Transducers; MEMS

1. Introduction

There are several kinds of ferroelectric materials that exhibit photovoltaic effects under near-ultraviolet illumination [1–3] that is shown in Fig. 1. The most outstanding advantage of the photovoltaic effect is its high output voltage over kV. This phenomenon of ferroelectrics is entirely different from that of the semiconductor p–n junction. This is because the photovoltaic effect occurs within the material and is considered to be an optical property of the material itself. The photovoltaic effect holds promise in the following areas: (1) high electrical output voltage over kV, (2) transducer from optical energy to electrical energy, and (3) wireless energy transfer. These characteristics are useful and applicable to micro-electro-mechanical systems (MEMS) [4–6].

Among such photovoltaic materials, lead lanthanum zirconate titanate is the most popular. Lead lanthanum zirconate titanate, i.e. $\mathrm{Pb}_{1-x}\mathrm{La}_x(\mathrm{Zr}_y\mathrm{Ti}_z)_{1-x/4}\mathrm{O}_3$ (abbreviated 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]. Some devices or systems that make use of photovoltaic material have been under development [8–12]. There have also been some reports from the material aspect [13–15]. Glass et al. explained that the photovoltaic effect was due to the non-equivalent excitation of electrons from the impurity level to the conduction band [16]. But there is no universal interpretation on the ferroelectric photovoltaic effect. There are, however, other problems, such as the slow response speed of the photostrictive effect around the second order due to the high electrical resistance of PLZT. In fact, the response speed of the photovoltaic current should be fairly fast in consideration of an electrical equivalent model [17,18]. It should be thus useful to fabricate improved output of the photovoltaic current in order to achieve fast-response devices. For this reason, a film structure is more useful than a bulk material in view of photovoltaic effect efficiency.

Recently, we have fabricated PLZT film on a trial basis and confirmed that the efficiency of the film structure was better than a bulk material. Our new structure design,

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[*] Corresponding author. Tel.: +81-29-861-7140; fax: +81-29-861-7167.
E-mail address: ichiki-m@aist.go.jp (M. Ichiki).

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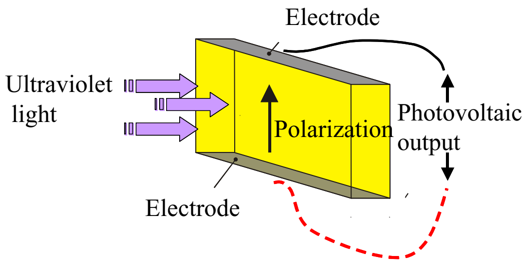

Fig. 1. Representation of photovoltaic effect of PLZT.

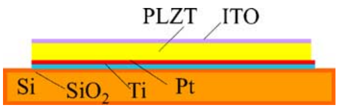

Fig. 2. Cross sectional view of layered PLZT film structure.

including a modified electrode configuration, was introduced into a layered PLZT film structure. We describe the sample preparation and its characteristics in the following sections. We will also present a phenomenological explanation of the improved photovoltaic effect on PLZT film.

It is necessary to sandwich the ferroelectric film structure with electrodes in order for its characteristics to appear. There are two possible locations for the electrode in the film structure. One has electrode sited beside the film and the other has the electrode sited at the upper and lower sides of the film. We chose the latter style for this experiment that is shown in Fig. 2 because it is suitable for the MEMS fabrication process and to decrease the poling voltage significantly. Since it is necessary to illuminate through the upper electrode, a transparent upper electrode was used.

2. Preparation of PLZT film

The PLZT film was formed using the metal organic deposition (MOD) method on Si-substrate, with the lower electrode sputtered onto the substrate. The Si-substrate was prepared using the standard MEMS process in our group [4–6]. The PLZT film was formed onto 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 chemical quantitative composition. The substrate was dipped into the liquid solution and rotated with a spin coater. Heat treatment was performed 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 procedure used in the sol–gel method [19]. These steps were repeated 10 times to form the film structure. Indium tin oxide (ITO) was sputtered to fabricate the upper electrode to estimate the photovoltaic effect and dielectric and ferroelectric properties.

Standard methods were used to estimate material characteristics: scanning electron microscopy (SEM) observation, X-ray diffraction (XRD) method, 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 already reported [20].

3. Experimental results and discussion

Fig. 3 shows a SEM figure of a crossed sectional figure of the formed film. The thickness of the film was 4 μm. The SEM inspection confirmed that the film structure was homogeneous. The interface between the lower electrode and the PLZT was flat and smooth without voids or deficiencies. The presence of a typical perovskite structure was confirmed with XRD that is shown in Fig. 4. No particular crystal orientation was observed and a random orientation was confirmed. The film had no pyrochlore or amorphous structure. Fig. 5a and b shows the photovoltaic voltage and current, respectively. The photovoltaic voltage had linear relationships with the illumination intensity. The photovoltaic voltage saturated to a constant value with increasing illumination intensity. These photovoltaic behaviors are based on the same mechanisms exhibited by bulk PLZT [14]. Photovoltaic voltage and current reached 0.8 V and 1.7 μA in the region of highest illumination intensity at 150 mW/cm^2. The

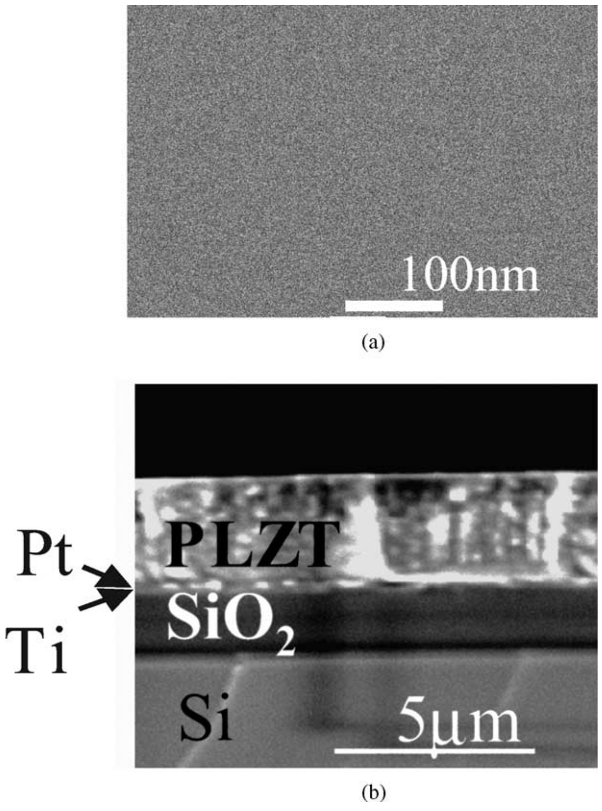

Fig. 3. SEM figure of (a) surface and (b) cross section of PLZT film structure.

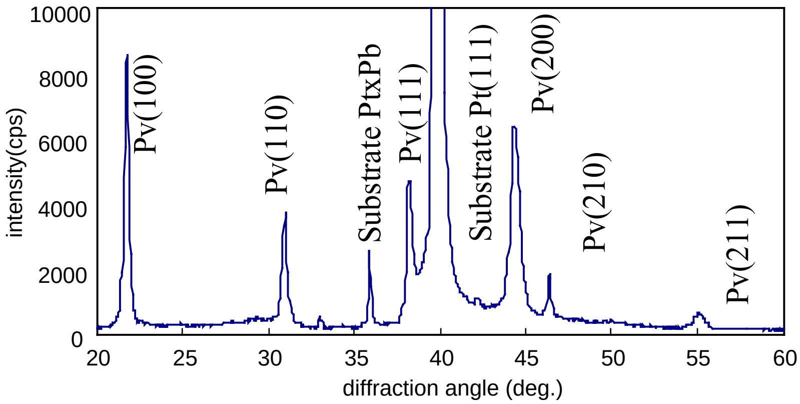

Fig. 4. X-ray diffraction profile of PLZT film structure.

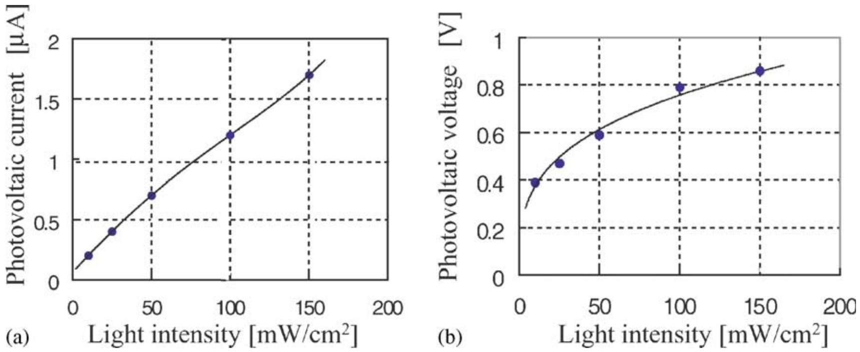

Fig. 5. Photovoltaic effect of layered PLZT film structure. Relationships between (a) photovoltaic current and (b) photovoltaic voltage and illumination intensity.

output level of the photovoltaic current of the PLZT film was three orders higher than that of bulk PLZT [21]. On the other hand, the photovoltaic voltage of the PLZT film was three orders lower than that of bulk PLZT [21]. Table 1 gives a comparison of PLZT in formed film and bulk condition [21]. The photovoltaic current of film per unit width was two orders higher than that of the bulk material due to the sample size.

Since bulk PLZT exhibits high photovoltaic voltage over kV and small photovoltaic current around nanoamere per square centimeter of area and millimeter of thickness, it is difficult to explore useful and practical applications with such an output level. These differences are due to the characteristics and also the configuration of the electrode. We will present a phenomenological explanation of the improved photovoltaic effect using a simple model. Fig. 6 shows bulk ceramics in (a), layered film in (b), and film element in (c). The width of the film element Δw is assumed to be 10 µm. Therefore, the real film is thoroughly connected with these film elements on the order of 10^3 times. As a result, the output of the photovoltaic current is 10^3 times that of a film element. It is assumed that the film element is illuminated from the side, while the sample is actually illuminated from the top. This assumption is valid in cases where

Table 1
Comparison of the photovoltaic properties of PLZT in bulk and layered film structure

	Bulk ceramics	Layered film structure
Sample width w (mm)	2.4	10.0
Sample height h (mm)	10.2	10.0
Sample thickness t (mm)	5.1	0.004
Polarization direction	Thickness	Thickness
Photovoltaic current (nA/cm)	16.8	1700
Photovoltaic voltage (V/cm)	2067	2150

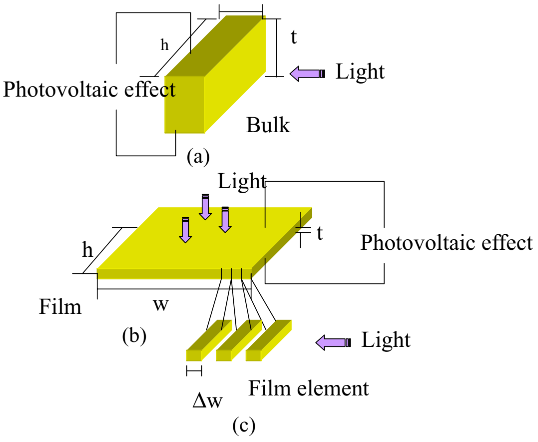

Fig. 6. Representative figure of illumination onto (a) bulk, (b) film, and (c) film element of photovoltaic materials.

the width Δw and thickness h of the thin film element are under 10 μm. This is because homogeneous illumination is achieved within such a scale. Since it is difficult to form film over 10 μm in thickness using present technology, this assumption is valid from a practical point of view. Screen printing technology enables us to form thicker film over 10 μm in thickness [22], but the film density is not high enough for sensor, actuator, and transducer applications.

A film structure is more easily poled and a homogeneous material condition easily and constantly achieved at a shorter electrode distance. This is also another advantage that makes for easy preparation of the film structure. Photovoltaic voltage has a linear relationship with the electrode distance, i.e. the thickness of film. On the other hand, since photovoltaic current only occurs from the illuminated film, the current is in proportion to the illuminated area of the film. This is one of the most outstanding advantages of using a film structure rather than bulk ceramics or single crystal. A layered PLZT film structure thus has controllable parameters: film thickness, illuminated area, and illumination intensity.

We have shown that a layered PLZT film structure has following advantages: (1) useful level of photovoltaic V and mA output, (2) several controllable parameters to modify output characteristics, and (3) easy formation of the film structure. 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 crystal, the advantages are quite clear. Therefore, a layered PLZT film structure, as proposed in this report, is more compatible with IT electronics and MEMS.

Our next target is to control the crystal orientation [23], heat treatment [24], and composition [25] for more improved characteristics and to achieve higher photovoltaic effect performance. Such a layered film structure could be useful as an energy transducer for optical to electrical conversion and would be applicable to micro and fast-rotating objects (e.g. ultrasonic motors) and MEMS devices.

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