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Micro Photo Detector Fabricated of Ferroelectric–Metal Heterostructure

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Abstract

The anomalous photovoltaic effect (APE) in ferroelectric thin films has been utilized for the development of an optical micro-detector active in the visible range (from 350 to 800 nm). La-doped $Pb(Zr,Ti)O_3$ (PLZT) ferroelectric films epitaxially grown on Pt(001)/Mg(001) substrate were fabricated into micro-detector arrays and characterized as to their optical response. The Au/PLZT/Pt/MgO device was self-polarized in the as-deposited form with the polarization vector perpendicular to film surface. The heterostructure photovoltage response ranged from 100 to 200 mV, and the photocurrent was ~30 nA/cm^2 for devices of ~250 μm diameter under illumination of 100 mW/cm^2 at wavelengths from 400 to 580 nm. Such micro-detectors can be used for optical sensors in MEMS devices as well as for electrical stimulators of biological cells.

Keywords

photo-detector; optical; ferroelectric; photo-voltage; thin-film

1. Introduction

Photovoltages as large as several kilovolts have been previously measured in poled ferroelectric materials under near-ultraviolet illumination.1›2) This anomalous photovoltaic phenomenon in ferroelectrics occurs within the material and is considered to be an optical property of the material itself.3›4) The photo-ferroelectric effect holds promise in various applications such as high electrical voltage output devices, optical-to-electrical energy transducers, and optical actuators. Most of these applications have been studied for ferroelectrics under UV irradiation. The photo-ferroelectric effect however spans a large wavelength range overlapping the visible spectrum. The high temperature and high chemical stability of many ferroelectric oxides coupled with a photo-response in the visible range have increased interest in their application in biological and space environments. Therefore, the photo-response properties of ferroelectric materials in the visible wavelength range are an important parameter to be investigated.

Most studies of the photo-ferroelectric effect has been undertaken in bulk materials such as Fe-doped $LiNbO_3$ and $BaTiO_3$ single crystals, and $BaTiO_3$ and $Pb(Zr,Ti)O_3$ (PZT) ceramics.5›6) The recent development of thin film deposition processes for oxide materials including ferroelectrics that result in the fabrication of atomically ordered oxide thin films and thin film heterostructures now allow for the study of a large class of ferroelectrics including those in the PZT class. $Pb(Zr,Ti)O_3$ (PZT) is the solid solution of $PbZrO_3$ and $PbTiO_3$. The morphotropic phase boundary (MPB) composition for Zr/Ti ~ 52/48 in PZT is

of interest because the co-existence of the tetragonal (T) and rhombohedral (R) phases leads to high polarizibility, high dielectric constant, maximized piezoelectric coefficients, and large photo-response. La doping into PZT can decrease grain size and fragmentation of polar domains, increase the fraction of regions adjacent to the domain walls increases the strength of the non-uniform internal electric fields,7) and increase carrier trapping in defects, hence enhancing photo response under illumination in the visible wavelength range.

In this article, we describe the fabrication of PLZT(100) heterostructures, the development of optical micro-photo-detectors from these heterostrctures, and characterization of their photovoltaic behavior as a function of wavelength and radiation intensity in the visible range.

2. Sample Preparation and Experimental

The ferroelectric photodetector is composed of a bottom electrode layer (typically platinum), an optically active La doped $PbZrTiO_3$ (PLZT) layer, and a partially transparent conducting top electrode layer (such as thin film Au or Pt). Since the photo-ferroelectric effect has been shown to be proportional to polarization, and polarization can be maximized through atomic order, epitaxial PLZT films were fabricated. To accomplish this, atomically ordered Pt(100) films (to act as bottom electrodes) of 200 to 500 nm thickness were epitaxially grown on a single crystal MgO(100) substrates by e-beam evaporation. Pt film growth conditions were optimized to yield a film on MgO with an XRD ϕ-scan of ~1° FWHM; this formed an excellent atomic template for epitaxial PLZT growth. The PLZT(100) ferroelectric layer deposition was carried out by pulse laser deposition (PLD) on top of a Pt(100)/MgO(100) structure at a temperature of 650°C by the use of a stoichiometric PLZT ceramic target and a KrF excimer laser (Lambda Physik, 248 nm in wavelength, 5 Hz repetition rate, 30 ns pulse width). The PLD was undertaken in a vacuum chamber with an ambient oxygen pressure of 250 mTorr. After growth of the PLZT film, a semi-transparent top electrode layer of Au or Pt was deposited on top of PLZT layer by e-beam evaporation or DC-sputtering.

The structure and morphology of the PLZT(100)/Pt(100) heterostructure were examined by X-ray diffraction (XRD) and scanning electron microscope (SEM). The ferroelectric properties of the dielectric PLZT layer were studied by capacitance–voltage (*C*–*V*) and hysteresis loop measurements using a Radiant Technology 6000HVS-5 ferroelectric test system. Isolated individual micro-photodectors configured in square and hexagonal arrays were fabricated by photolithography and etching of the Au/PLZT/Pt(100) heterostructure. Microdetector size was varied from 50 to 500 μm in diameter with the top electrode (Au or Pt) of 10–20 μm smaller diameter than that of micro-detectors. The photo response of the heterostructure and isolated micro-detectors was then examined by both AC, and DC measurements under illumination by a xenon discharge lamp, a mercury lamp, and a solar simulator source.

3. Results and Discussion

PLZT thin films grown on top of the (100) oriented Pt film bottom electrode were identified to have a perovskite structure with (100) crystallographic orientation normal to the growth surface, as shown by the XRD θ–2θ scan in Fig. 1(a). The PLZT films were also shown to be fully ordered in the plane as defined by the pole figure plots from GAADS in Fig. 1(b) showing a ~1° FWHM. The ferroelectric properties of the PLZT films were evaluated from measurement of the *D*–*E* hysteresis loop, as shown in Fig. 2. For the 1 μm thick epitaxial PLZT film, a remnant polarization Pr of 25 $\mu C/cm^2$, and a coercive field Ec of 1×10^5 V/cm were obtained without any poling process. Hence the “as grown” PLZT films exhibited a “self-poling” behavior. Since the photo-ferroelectric effect is proportional to polarization for

ferroelectric material, the effect of "self-polarization" (large Pr), accompanying epitaxial film growth of ferroelectrics8,9) will be of great benefit to ferroelectric photo-detector fabrication and applications.

Optical characterization of the ferroelectric film in the visible range was performed by measuring the photovoltage and photocurrent of PLZT in a Pt(Au)/PLZT/Pt hetero-structure device under irradiation by a xenon lamp and a solar simulator source. The spectral response of a device with a 500 μm diameter top electrode under uniform illumination of a xenon discharge lamp in combination with a monochromator is shown in Fig. 3. The output of the xenon discharge lamp/monochromator system was set to a power density of ~5 mW/cm^2, and was used in combination with a chopper at a frequency of 10 Hz, and a lock-in amplifier for data acquisition. Figure 3 shows, the optical output of the detector with a well pronounced peak in the mid-visible range and a sharp increase at the lower end of visible range approaching the ban-gap of PLZT at about 300 nm (corresponding to ~3:5 eV). The measured responsivity is ~10^3 V/W.

Measurement of the microdetector DC output was also made under illumination from a solar simulator source and was recorded by an electrometer (Keithly 6517A). The solar simulator source emitting a near continuous solar spectrum was calibrated with maximum power density to 130 mW/cm^2, which corresponds to the intensity received on the earth's surface on a clear day at noon. The responsivity of the ferroelectric photovoltaic device versus radiant intensity was plotted in Fig. 4 for the same device as in Fig. 3. The DC measurement shows responsivity of ~10^2 V/W with voltage output increasing with light intensity from 0 to ~120 mV at 130 mW/cm^2. The DC output of the micro-detector as a function of wavelength using the monochromator and the Xenon lamp also resulted in a responsivity of ~ 10^3 V/W at 600 nm.

The photovoltaic effect in non-centrosymmetric ferroelectric materials has been previously discussed with no universal interpretation.4,5) Recent studies have reported that a large number of photo-induced carriers can be created by high irradiation of polar materials. In addition, photo induced centers, including shallow levels of Ti^{3+} (~50 meV), and deep levels of Pb^{+} and Pb^{3+} (~2 eV), are generated near a lanthanum impurity.7) Since these Ti/Pb centers are in the band gap, their creation and recombination processes will have a contribution to the photovoltaic effect under illumination by visible light. Further, the doped-La impurities can themselves act as local potential wells since they can substitute for both the Pb^{2+} and partially Ti^{4+} ions in PLZT displacing the neighboring ions and forming defects in the lattice. The electrons, which are exited from the impurity centers by radiation of suitable wavelength, are re-trapped at other locations, leaving behind positive charges of ionic trap centers in the non-central polar PLZT system. The resulting space charge field7) between the positively ionized centers and the trapped negative charges modulates the local potential distribution, and results in an internal field which gives rise to a volume photovoltaic effect. The resulted photovoltage linear relationship with irradiation intensity and its approach to a saturation value at high intensities shown in Fig. 4, exhibit the same mechanism as in bulk PLZT.2,10) Given the measured strong optical response in PLZT heterostructures, and given the chemical and structural robustness of PZT-bond ceramics, it is of interest to identify applications for their ceramic photo-detectors. Such applications can rely heavily on the relevant character of the devices and includes photo-detector applications in harsh environments such as in space or biological systems. The optical response of the microdetector and its oxide composition point to possible applications where chemically robust materials (*e.g.*, oxides) are required for photo activation of biological response. Such applications include studying the mechanism of interaction of electromagnetic fields with biological tissues,11) simulating the transmembrane voltage induced in cells with different shapes,12) and electrical stimulation of retinal neurons.13,15)

For biological applications the thin film heterostructures were fabricated into small single isolated microdetectors of 200 μm diameter with a top electrode of about 20 μm less than the size of the detector by photolithographic processing and dry etching. The optical output of individual micro-detectors was measured by positioning recording electrodes near the top and bottom electrodes of the device, as shown in Fig. 5. Glass micropipettes filled with 100 mM K+ gluconate used for its relative good conductivity and ease of handling were positioned near the device electrodes, and small droplets of the conducting liquid were forced from the tip of the pipettes to make contact with the electrodes. Responses were measured with an Axon instrument patch clamp amplifier in resistive feedback mode. Current and voltage signals were filtered on the amplifiers at 2 kHz and sampled at 10 kHz using a PCI-M1016XE data acquisition board from National Instruments.

The photovoltage response development of an isolated PLZT micro-device was measured using long light pulses at a saturation intensity level of 400 mW/cm^2 as obtained from a white light LED. The output signal, as shown in Fig. 6(a), exhibited transient and steady state components. It sharply increased to a maximum and then relaxed to a stable value with the light-on. Upon turn-off the light, the microdetector experienced a similar relaxation process until reaching the zero output level. The transient photo response has pyro-electric origin and decays with the thermal relaxation time of the crystal as well as the relaxation time of the circuit used to measure the output. The response/relaxation time of the pyroelectric is of the order of 1 ms as can be seen in Fig. 6(b). With the resistance of access through the pipette about 2 MΩ16) and the typical capacitance of the micro-detector of the order of 1 nF, the measured time constant of ~1 ms is in good agreement with the RC time constant calculated based on these data. Such time response values are close to those seen in *in-vitro* cell experiments that applied pulses to neurons and recorded the current and response time (a few milliseconds) of the neurons in a voltage-clamp experiment.17)

The photovoltaic behavior of an isolated PLZT micro-detector shown in Fig. 6 is similar to that of the planar Pt/PLZT/Pt detector given in Fig. 4, but with lower voltage output. This may be a result of the patterning and etching process, which is set to be optimized.

4. Conclusion

In conclusion, the anomalous photovoltaic properties of PLZT thin films have been investigated in terms of optical intensity and wavelength from near ultraviolet throughout the visible range. The photo-response of PLZT shows activities in the visible range with a peak at ~650 nm and nonlinear radiation intensity dependence, reaching a significant saturation value at high illumination intensity. Devices made from such photo active ceramics may find use in biological systems where the chemical robustness of oxides and the optical activation allow for excitation of cells such as retinal neurons.

Acknowledgments

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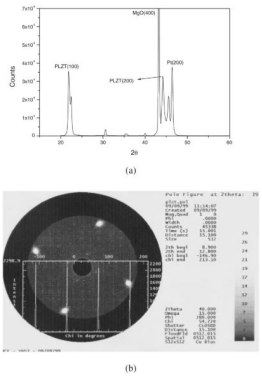

Fig. 1.

(a) An X-ray diffraction 2θ spectrum of a PLZT/Pt/MgO heterostructure microdetector indicating (100) atomic ordering of the PLZT active oxide layer grown on (100) ordered Pt, and (b) Pole figure from PLZT/Pt/MgO heterostructure confirming the planar 4-fold symmetry of PLZT film structure.

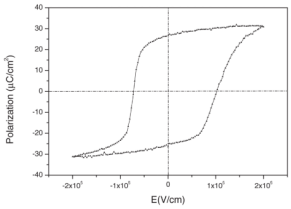

Fig. 2.

Hysteresis loop measured using the Sawyer–Tower method indicating a remnant polarization of 25 μC/cm^2, and a value of 10^5 V/cm for the coercive field.

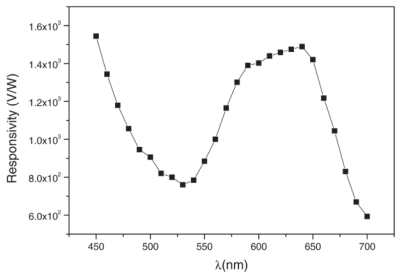

Fig. 3.
Spectral response of a 500 μm diameter PLZT micro-detector using a xenon lamp with monochromator output set at ~5 mW/cm^2.

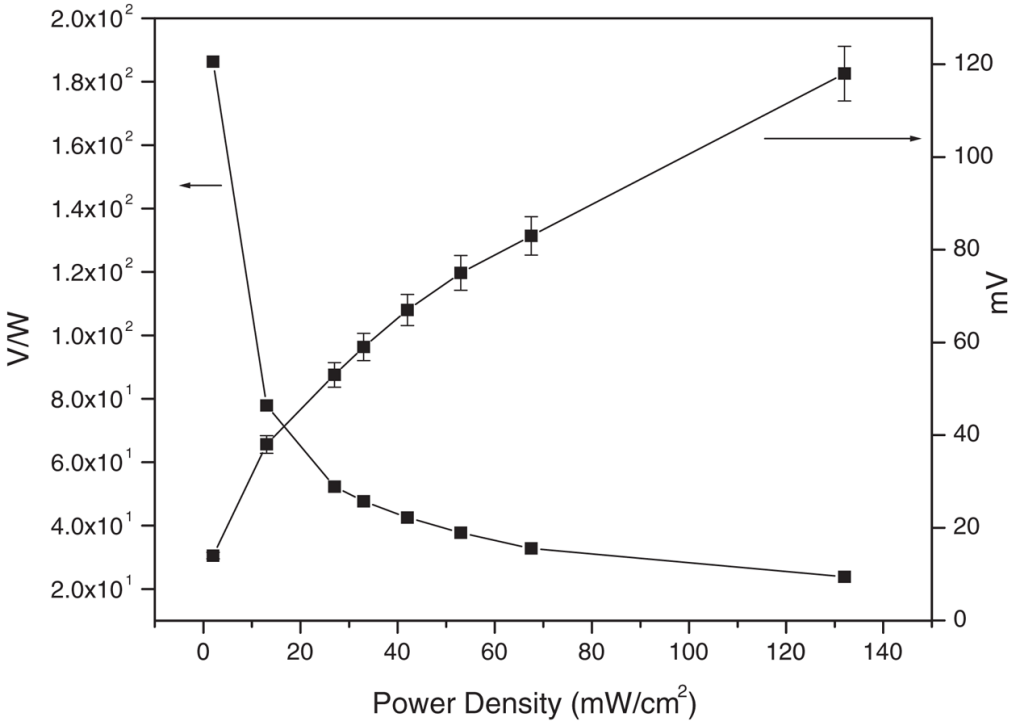

Fig. 4.

Photovoltaic output, and the responsivity of a 500 μm diameter thin film microdetector as a function of intensity of a solar simulator source.

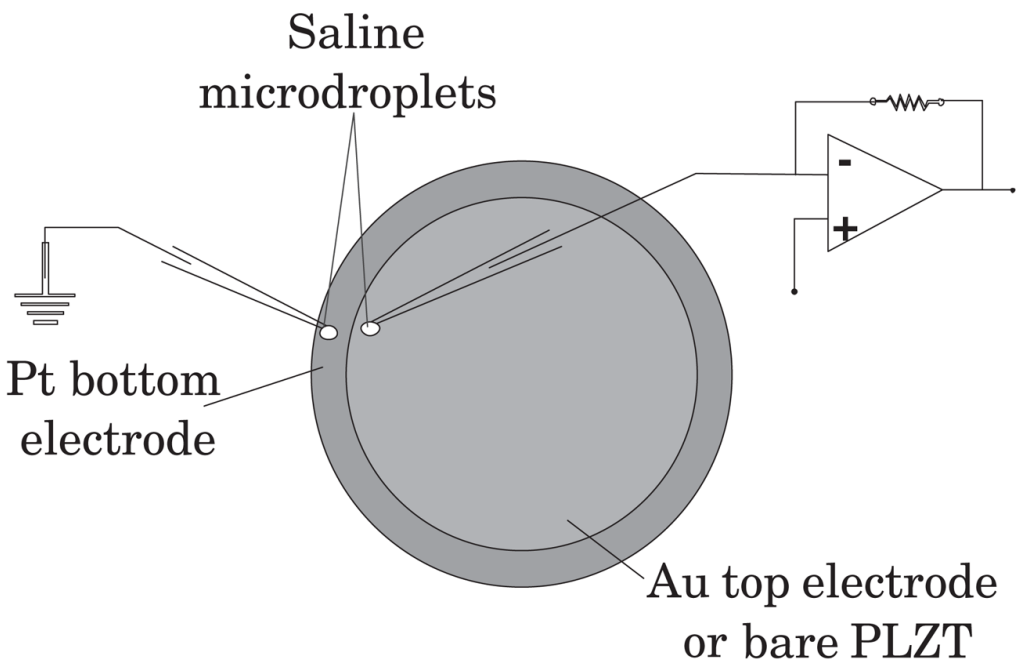

Fig. 5.
Schematic drawing of the patch-clamp set-up for optical output measurement of an isolated microdetector.

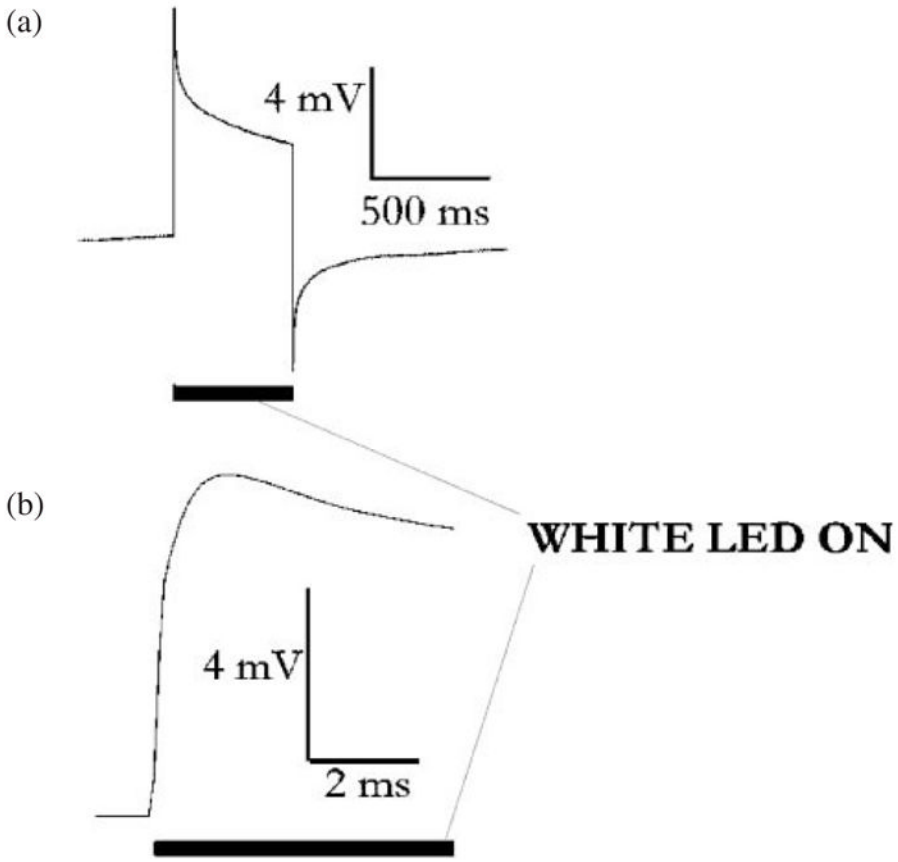

Fig. 6.
Response value and response time of an isolated 200 μm micro-detector upon radiation with 440 nm light of white LED at an intensity of 400 mW/cm^2.