Infrared Physics & Technology 71 (2015) 1–9

Contents lists available at ScienceDirect

Infrared Physics & Technology

journal homepage: www.elsevier.com/locate/infrared

Modified lead titanate thin films for pyroelectric infrared detectors on gold electrodes

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HIGHLIGHTS

- Pyroelectric modified lead zirconium titanate (PZT) thin film on gold surface.
- Pyroelectric lead calcium titanate (PCT) thin films on gold surface.
- Pulsed laser ablation of modified lead titanate thin films for infrared detection applications.
- Measured pyroelectric and dielectric properties.
- Demonstrate poling and increment of pyroelectric coefficient.

ARTICLE INFO

Article history:
Received 3 September 2014
Available online 5 March 2015

Keywords:
Lead calcium titanate
Lead zirconium titanate
Pulse laser deposition
Gold electrode

ABSTRACT

Pyroelectric infrared detectors provide the advantage of both a wide spectral response and dynamic range, which also has enabled systems to be developed with reduced size, weight and power consumption. This paper demonstrates the deposition of lead zirconium titanate (PZT) and lead calcium titanate (PCT) thin films for uncooled pyroelectric detectors with the utilization of gold electrodes. The modified lead titanate thin films were deposited by pulsed laser deposition on gold electrodes. The PZT and PCT thins films deposited and annealed at temperatures of 650 °C and 550 °C respectively demonstrated the best pyroelectric performance in this work. The thin films displayed a pyroelectric effect that increased with temperature. Poling of the thin films was carried out for a fixed time periods and fixed dc bias voltages at elevated temperature in order to increase the pyroelectric coefficient by establishing a spontaneous polarization of the thin films. Poling caused the pyroelectric current to increase one order of magnitude.

1. Background

Pyroelectric detectors utilize materials that possess a temperature dependent spontaneous polarization. This spontaneous polarization exists for temperature less than Curie temperature of the material. Incident radiation heats up the detector, expanding the crystal lattice and changing the electric polarization (P) of the material. The change in electric polarization varies the surface charge with temperature. The surface charge is sampled with electrodes so heating results in a current flowing onto or off of the detector. The detector can be modeled as a capacitor filled with a ferroelectric, pyroelectric material. Ferroelectric crystals possess a spontaneous polarization. The pyroelectric effect is observed when the spontaneous polarization changes with the temperature. Another effect of temperature variation is that, it causes a proportional change in the dielectric constant of the capacitor [1].

Pyroelectric thin films can be used in uncooled infrared detection for night vision and instrumentation applications. Typically the detectors are designed to detect radiation in the 8–14 μm wavelength band. The thermometer which changes temperature through heating by the absorbed infrared radiation is suspended above the substrate by micromachining as shown in Fig. 1. This reduces the heat lost by conduction to the substrate and allows for the formation of an optically resonant cavity. Surface micromachining is a convenient method for fabrication the detectors. In this case the thermometer is fabricated on an amorphous sacrificial layer. To emulate this situation, the pyroelectric capacitors were fabricated on an amorphous silicon nitride layer resulting in polycrystalline electrodes and modified lead titanate thin films.

The pyroelectric coefficient p is the measure of the rate of change of the electric polarization (P) with temperature and is defined as [1]:

$$p \equiv \frac{\partial P}{\partial T} \tag{1}$$

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http://dx.doi.org/10.1016/j.infrared.2015.01.028

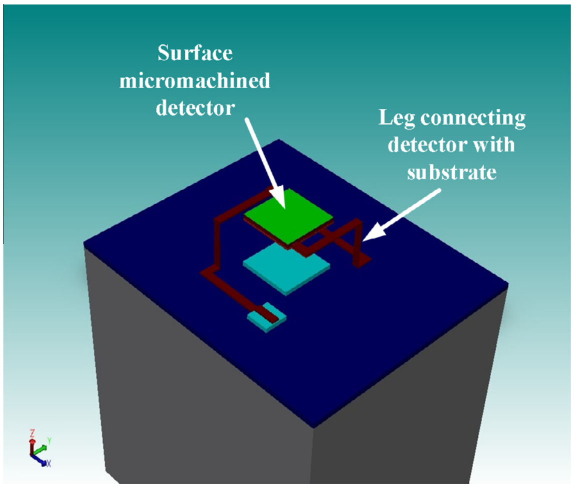

Fig. 1. Design of an infrared detector where modified lead titanate could be used as a detecting material.

A larger pyroelectric coefficient provides a larger pyroelectric current and thereby response from a thermal infrared detector.

The pyroelectric current (i_p) can be calculated using the pyroelectric coefficient using the following equation [1]:

$$i_p = p\frac{dT}{dt}A_d \tag{2}$$

where A_d is the electrode area sampling the change in electric polarization and through which the pyroelectric current flows.

Modified lead titanate is considered an important thin film ferroelectric material that exhibits high permittivity, large spontaneous polarization and pyroelectric current, electro-optic, and ferroelectric effects. These properties lead themselves to a wide range of applications such as dynamic random access memory, sensors, actuators, accelerometers, and optical switches [2]. The high pyroelectric coefficient of modified lead titanate depends upon the growth of a high quality, ferroelectric perovskite structure [3]. Lead zirconium titanate has two phases: intermediate pyrochlore phase and the ferroelectric perovskite phase [4]. The formation of the desired perovskite phase depends on the deposition technique including the process temperature, ambient pressure, and substrate [3–5]. Pulsed laser deposition has demonstrated to be a successful method for fabrication of high-quality lead titanate thin-film materials [6,7]. In our earlier work [8] we have demonstrated deposition and X-ray diffraction of lead zirconium titanate ($PbZr_{0.4}Ti_{0.6}O_3$) (PZT) and lead calcium titanate ($Pb_{0.7}Ca_{0.3}$ TiO_3) (PCT) thin film grown by pulsed laser deposition at 650 °C and 550 °C respectively. We also measured the variation of capacitance and loss tangent with temperature, variation of pyroelectric coefficient with temperature and pyroelectric current with time. Besides these, in [9], we have also demonstrated the effect poling increased the pyroelectric coefficient for both PCT and PZT thin films. In this work, the deposition of modified lead zirconium titanate ($PbZr_{0.4}Ti_{0.6}O_3$) (PZT) and lead calcium titanate ($Pb_{0.7}Ca_{0.3}Ti0_3$) (PCT) at various temperatures by pulse laser deposition, resulting in the growth of the polycrystalline perovskite structure, has been investigated. Capacitors were fabricated to measure the dielectric properties and pyroelectric current of the deposited modified lead titanate films with temperature. The paper also reports on the dependence of dielectric constant and loss tangent of PZT film grown at different temperatures and PCT films grown at different energies. We have also studied the pyroelectric current and pyroelectric coefficient variation with temperature and time respective for PZT and PCT film grown at different conditions. We have described the effect of bias voltage and time on the poling of ferroelectric PZT and PCT films. The pyroelectric current measurement was done for the films and corresponding pyroelectric coefficients were calculated. For one PZT and one PCT film grown at 650 °C and 550 °C respectively, the pyroelectric current measurement was done for 10 cycles in order to check the repeatability of the measurements.

2. Thin film fabrication

The fabrication was started with the deposition of 400 nm-thick Si_3N_4 passivation layer on top of a ⟨100⟩ *p*-type silicon wafer by AJA rf-sputtering system at 150 W rf power and 5.5 mTorr of Ar gas environment at room temperature. After that, 20 nm of Ti was deposited on top of the passivation layer at 150 W rf power and 10 mTorr of Ar gas environment in the custom sputter tool. This layer serves as the adhesion layer for the bottom Au electrode. The 100 nm-thick Au layer was deposited at 150 W rf power and 10 mTorr of Ar gas environment. This layer not only serves as the bottom electrode for the capacitor but serves for the crystallization of PZT/PCT films.

After that, laser ablation of the PZT film was carried out using a KrF excimer laser with a wavelength of 248 nm, repetition rate 10 Hz and pulse laser deposition up to 500 mJ at 200 mTorr of O_2 gas environment. The temperature of the chamber was varied from 500 °C to 650 °C and annealed at the same temperature as the deposition temperature but varying the annealing time at 5 min and 10 min to form the polycrystalline perovskite structure of the PZT film. The film structure was characterized by the X-ray diffraction technique which will be discussed in the next section. The deposition of PZT film grown by pulsed laser deposition at 650 °C and annealed for 10 min at 200 mTorr O_2 gas environment and 500 mJ energy showed ferroelectric perovskite structure and this film was used for the fabrication of capacitors. The thickness of the PZT layer was measured with an Ellipsometer-Gaertner-LS300 and the thickness was found to range from 250 nm to 347 nm. Then, 100 nm of Au layer was deposited at 150 W rf power and 10 mTorr of Ar gas environment and patterned by lift-off technique to form the capacitor structures.

In order to deposit the PCT films, laser ablation of the PCT film was carried out using a KrF excimer laser with a wavelength of 248 nm, repetition rate 10 Hz and pulse laser deposition up to 175 mJ at 200 mTorr of O_2 gas environment. The energy of the excimer laser was varied from 125 to 175 mJ and annealed at same temperature of the deposition but varying the annealing time at 10, 15 min and 20 min to form polycrystalline perovskite structure of PCT film. The deposition of PCT film grown by pulsed laser deposition at 550 °C and annealed for 10 min, 200 mTorr O_2 gas environment and 175 mJ energy showed ferroelectric perovskite structure and this film was used for the fabrication of capacitors. The thickness of the PCT layer was also measured with the Ellipsometer-Gaertner-LS300 and was found to range from 220 nm to 244 nm.

The AFM macrograph of the deposited PZT film at 650 °C and annealed for 10 min at 200 mTorr O_2 gas environment is shown in Fig. 2(a). The AFM macrograph of the deposited PCT film at 550 °C and annealed for 10 min at 200 mTorr O_2 gas environment is shown in Fig. 2(b).

3. Characterization

The X-ray diffraction of the samples was done in a Siemens D500 powder diffractometer, which was equipped with a Cu-Target producing *x*-rays at 1.54 Å. The rate of scan is determined by the step time and the dwell time. Here the step time was 0.01 s and the dwell time was 0.4 s. The scan range was the range