Materials Science in Semiconductor Processing 105 (2020) 104723

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Ferroelectric PZT thin films for photovoltaic application

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ARTICLE INFO

IndexTerms:
Lead zirconium titanate
Chemical deposition
Ferroelectric
Polarization
Photovolataics

ABSTRACT

The ferroelectric photovoltaic response characteristics of Lead Zirconate Titanate (PZT) thin film in metal-ferroelectric-metal (MFM) configuration is studied under 33 mode upon exposure to UV radiations. PZT thin films of 180 nm are prepared on inter-digital electrodes patterned silicon substrate (with silicon dioxide as insulating layer) using chemical solution deposition (CSD) technique followed by rapid thermal annealing. PZT thin films are found to be in single phase and possess high electrical polarization (50μC/cm^2). Significant increase in photocurrent and large value of open circuit voltage (1.0 V) is observed for the prepared ferroelectric photovoltaic film under UV illumination.

1. Introduction

Because of the drastic requirements for renewable solar energy, researchers are now considering novel materials for improving the performance of photovoltaic (PV) devices. PV is the most fascinating ways of converting, natural solar energy to electrical energy and helps in reducing the dependence on non renewable sources. Recently, the interest in ferroelectric photovoltaic devices has renewed [1], and ferroelectric properties are tailored to enhance its efficiency and to reduce the cost. This phenomenon has been reported for various ferroelectric perovskite thin films including Lead Zirconium Titanate (PZT) [2], Barium Titanate (BT) [3], Lithium Niobate (LNO) [4], and Bismuth Ferrite (BFO) [1]. Among various ferroelectric materials, PZT is one of the most promising candidates because of its unique characteristics including good ferroelectric properties, high piezoelectric coefficient and superior dielectric properties which support the ferroelectric photovoltaic [5–7].

In literature, few reports are present on the photovoltaic study of PZT thin film in metal-ferroelectric-metal (MFM) capacitor configuration, and promising photo response characteristics have been reported [2,8,9]. Yang et al. [8] and Ocala et al. [9] have studied the photocurrent of sol-gel derived PZT thin films, however, they were unable to explain the short circuit current and open circuit voltage which are very crucial parameters for photovoltaic study. Similarly, Kholkin et al. [10] have also demonstrated PV effect in PZT thin film grown by spin coating technique, but the results are not encouraging for device application. Since photovoltaic effect is the surface dominating phenomena, the exploitation of inter digital electrodes (IDEs) seems to be more advantageous for preparation of photovoltaic cell instead of capacitor configuration. IDEs may enhance the response as well as efficiency due to efficient collection of photo-generated carriers [11]. However, no report is available in the literature on photovoltaic study of PZT thin film using IDEs. Therefore, in the present study, PZT thin films have been grown on the substrate having pre-patterned IDEs with an objective to achieve an enhanced open circuit voltage and short circuit current.

2. Experimental

Fig. 1 shows a brief schematic of photovoltaic measurement setup along with the detailed specification of the photovoltaic device. For Photovoltaic application, inter-digital electrodes (IDE) of platinum (Pt) have been patterned on (100) silicon (Si) wafer with silicon dioxide as insulating layer using conventional photolithography technique (Fig. 1). Prior to deposition, substrates were well cleaned with trichloro ethylene, acetone and iso-propyle alcohol. The insulating layer (silicon dioxide) of 2 μm thick was grown using thermal oxidation. The deposition of platinum was carried out by RF magnetron sputtering technique using 3” diameter platinum target (99.99% pure) at 10 mTorr sputtering pressure in 100% argon ambient and 30 W rf power. Subsequently, IDEs of Pt with line width and line spacing of 500 μm each with 8 mm finger length (overlapping length) were patterned on Si using photolithography technique in clean room environment.

Lead Zirconium Titanate (PZT) thin films with composition as

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https://doi.org/10.1016/j.mssp.2019.104723
Received 15 March 2019; Received in revised form 25 July 2019; Accepted 4 September 2019
Available online 12 September 2019

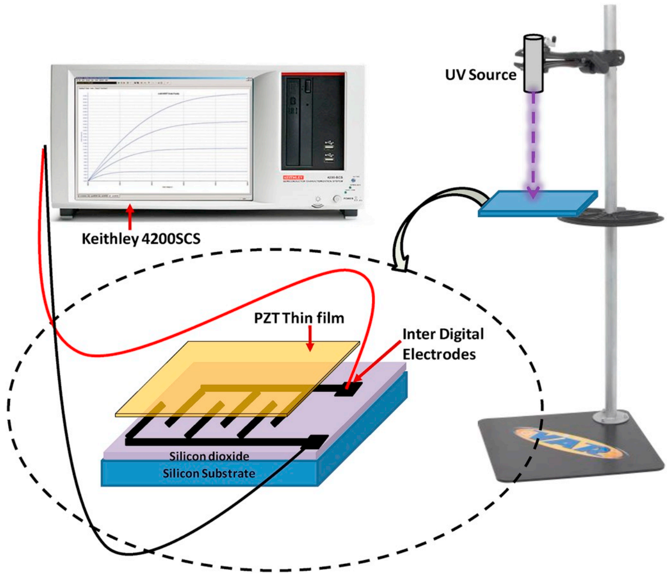

Fig. 1. Experimental setup for the Photovoltaic study with the detailed schematic of the photovoltaic device having PZT thin film deposited on platnized IDEs over silicon substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$Pb_{1.1}(Zr_{0.6}Ti_{0.4})O_3$ were prepared on IDEs/SiO_2/Si wafer by using chemical deposition technique using lead(II) acetate ($(PbCH_3COO)_2$), zirconium (IV) isopropoxide ($Zr((CH_3)_2CHO)_4{\cdot}(CH_3)_2CHOH$), and Titanium isopropoxide ($Ti\{HCO(CH_3)_2\}_4$) as raw materials [12]. The PZT thin film was deposited by spin coating PZT sol at the speed of 3000 rpm for the duration of 30 s followed by pyrolysis on a temperature controlled hot plate at 300 °C temperature. 1 μm thickness of PZT film was achieved by repeated coating of the sol on IDEs/SiO_2/Si wafer. Crystallization of PZT film in perovskite phase was achieved by rapid thermal annealing at 650 °C for 25 min. The deposition of PZT thin film using chemical route described above produces high quality and crack free films.

X-Ray Diffraction (Rigaku, Ultima 4) with Cu Kα radiations was used to study the crystallographic orientation and crystallinity of thin film. UV–Visible spectrophotometer (PerkinElmer lamda 35) was utilized to investigate the optical property of PZT thin film. The ferroelectric properties of the CSD grown PZT film have been studied by measuring the hysteresis loop (PE loop traser, Radiant, ferroelectric measurement system). The electrical property and photovoltaic characteristics were studied using semiconductor characterization unit (Kiethly 4200 SCS).

The photovoltaic response was measured utilizing near-UV light of wavelength 365 nm for illumination along with semiconducting characterization unit as shown in Fig. 1. The UV radiations were illuminated from top side of the metal-ferroelectric-metal (MFM) structure of photovoltaic device using mercury arc lamp (with light filters). The dynamic response was also investigated as a function of time in repetitive on/off mode of UV light. The photoinduced current and voltage were respectively, measured under short circuit and open circuit conditions using SCS 4200.

3. Results and discussion

The structural property of the CSD deposited PZT thin film grown on platnized silicon substrate is analyzed using X-Ray diffraction pattern as shown in Fig. 2. The PZT thin film annealed at 650 °C is observed to be polycrystalline having crystallites oriented along (100), (110), (111), (200) and (211) reflection planes. Absence of peak corresponding to any secondary phase (Fig. 2) indicates the formation of pure perovskite

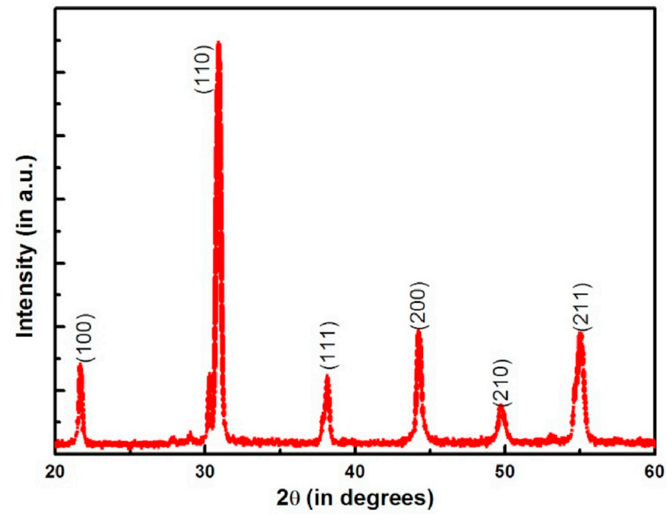

Fig. 2. X-Ray diffraction pattern of PZT thin film annealed at 650 °C for 30 min.

phase of PZT. The observed XRD pattern matches well with the literature reports showing the formation of rhombohederal structure [13] with Zr and Ti atoms at B-site, Pb atoms at A-site, and oxygen atoms at the face center of the unit cell. The lattice parameter and the interplanar spacing of the PZT film annealed at optimized temperature are found to be 4.09 Å and 2.89 Å respectively. The average crystallite size obtained using Scherrer's Formula from full width at half maximum value of the dominant (110) XRD peak is about 26 nm [14]. The stress modulus [15] in the PZT thin film can be estimated using $(a\text{-}a_o)/a_o$ in percentage, where ‘a’ and ‘a_o’ are the lattice parameter corresponding to thin film and bulk material respectively. The stress modulus is found to be 0.9% which may arise due to the presence of defects in the deposited PZT thin film. The calculated value of band gap as measured from the UV–Visible optical transmission spectra for PZT thin film is 3.6eV which is close to the corresponding value (3.7eV) reported for bulk as mentioned in our previous reports [16,17].

The ferroelectric behavior of PZT thin film has been confirmed by the room temperature hysteresis loop (PE loop) measurements between polarization (P) and electric field (E) obtained under the applied electric field up to 170 kV/cm at a frequency of 1 kHz (Fig. 3). The

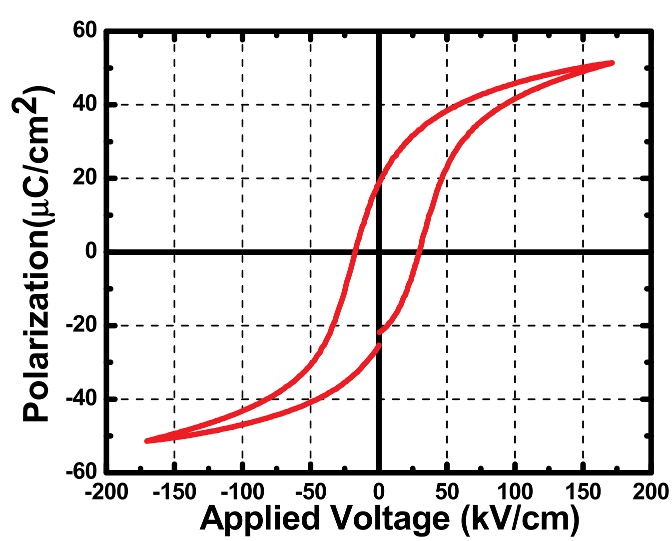

Fig. 3. Polarization-Electric field (PE) hysteresis loop of the PZT thin film deposited on platinised silicon substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

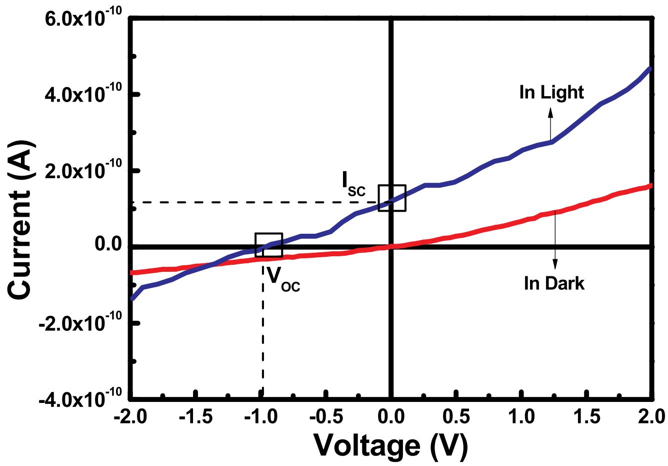

Fig. 4. Current-Voltage characteristics of the PZT thin film based photovoltaic cell using Pt IDE, under both dark condition and with illumination of UV light.

hysteresis loop of the PZT thin film grown at 650 °C is well defined and was found to be slim and symmetric (Fig. 3), indicating the growth of ferroelectric PZT thin film. The remnant polarization, saturation polarization and coercive field are found to be 20μC/cm^2, 50 μC/cm^2 and 20 kV/cm respectively, which are in agreement with the corresponding values reported in literature [18].

The current-voltage characteristics of PZT thin film based photovoltaic cell (schematic shown in Fig. 1) were recorded under both the dark condition and with the illumination of UV radiation using Pt IDEs, and are shown in Fig. 4. The observed behavior of current-voltage characteristics is imputed to the existence of ferroelectric photovoltaic effect. The dark current increases almost linearly (0–1.62 × 10^{-10} A) with increase in applied bias up to 2.0 V and is found to be symmetrical about both positive and negative polarity of applied bias. Significant change in the IV characteristic of photovoltaic cell has been observed under illumination of UV radiations (Fig. 4). The photocurrent was found to increase significantly (1.2 × 10^{-10} A to 4.63 × 10^{-10} A) over entire measured range of applied bias (0–2 V). Furthermore, IV characteristic under UV illumination was found to be asymmetrical, in contrary to that obtained under dark condition (Fig. 4). The drastic variation in current in the presence of UV radiation is not only because of energy band gap but also due to the presence of polarization. When the incident ultra violet light of 365 nm wavelength correlating to the energy band gap falls on PZT thin film which is electrically poled using corona poling in MFM configuration, the ferroelectric thin film absorbed photons by virtue of which the charge carriers are generated constituting of electrons and holes. Due to the presence of ferroelectric properties in PZT thin film, a polarization induced internal electric field called depolarizing field exists, which splits the photo generated electron-hole pairs apart. The photo-generated electrons and holes are propelled by the internally built electric field which is in opposite directions towards the anode and cathode respectively. Interdigital electrodes underneath PZT ferroelectric thin film acts as a various capacitors arranged in parallel. Due to the presence of inter digital electrodes, each capacitor element has its own polarization which differentiate the photogenerated electrons from holes. This furnishes the path for the generated electrons and holes to move towards electrodes. Therefore at a fixed bias, the enhanced photocurrent and asymmetricity in the IV characteristics is obtained under UV illumination (Fig. 4).

As observed from Fig. 4, the open circuit voltage (V_{oc}) and short circuit current (I_{sc}) for the prepared photovoltaic cell are found to be about 1.0 V and 1.2 × 10^{-10} A respectively. The power conversion efficiency (η) is calculated using $\eta = \frac{V_{Oc}J_{Sc}}{P_{in}} \times 100$, where V_{OC}, J_{SC} and P_{in} are open Circuit Voltage, short circuit current density and input power respectively. The power conversion efficiency calculated in the present

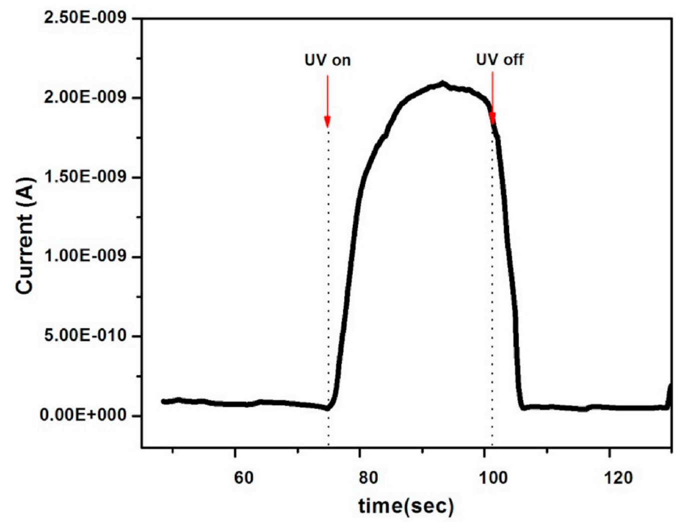

Fig. 5. The transient response of photocurrent of PZT thin film based photovoltaic cell measured at a fixed bias of 5 V as a function of time with switching of light illumination on and off.

work is found be slightly low and is found to be 2.6 × 10^{-3} (in percentage). The low value of power conversion efficiency is may be due to the presence of highly insulating nature of PZT film. The obtained value of V_{OC} is reasonably high in comparison to the corresponding values reported for ferroelectric photovoltaic cells by other workers [10]. The large amount of open circuit voltage in the presence of UV light may be attributed to the utilization of inter digital electrode configuration for the ferroelectric photovoltaic cell in the present study, besides good ferroelectric property of the deposited PZT thin film. The transient response of the prepared cell is shown in Fig. 5 as a function of time. In the transient response, the UV light is allowed to fall on the photovoltaic cell for the interval of 30 s. Initially the dark current (without UV illumination) was of the order of 10^{-12} A. The built in electric field present in the ferroelectric thin films through out the bulk region originating from electric polarization is not completely cancelled out by screening charges. Thus, photovoltaic effects can be explored in ferroelectric materials without the requirement of p-n junction. Also, the conversion of light energy into electrical energy in photovoltaic systems reckons on a form of built-in asymmetry that leads to the separation of photo-generated electron hole pairs. The anomalous ferroelectric photovoltaic effect observed in polar ferroelectric materials is due to their inherent non-center symmetrical structure which plays a pivotal role in this mechanism [19]. Under the illumination of UV light, the order of current was found to increase from 10^{-12} A to 10^{-9} A at a fixed applied bias of 5 V and attains a saturated value of photocurrent as shown in Fig. 5. The PZT thin film based photovoltaic cell exhibits an increase in the current by three orders in magnitude on exposure to UV radiation. Subsequently when UV illumination is off (Fig. 5), a fast fall in photocurrent is observed and photovoltaic cell regains the original value of dark current. The observed enhancement in the photocurrent is due to the combined effect of novel design of photovoltaic cell having IDEs and growth of good quality of PZT thin film exhibiting enhanced ferroelectric photovoltaic effect. Further, the fast fall time in photocurrent observed in present work confirm the growth of PZT film with minimal defects and resulting in recombination of photo-generated electrons and holes quickly when light source was switched off. This indicates the fast switching characteristics of ferroelectric domain in the deposited PZT thin films. The photovoltaic response has also been measured for the unpoled sample, however response was found to be negligible. Therefore, poling plays crucial role in attaining an efficient UV response.

4. Conclusion

Single phase and good quality Lead Zirconate Titanate (PZT) thin film has been successfully deposited by chemical solution deposition technique and a ferroelectric photovoltaic cell was prepared by using platinum inter digital electrodes. The PZT thin film exhibits good ferroelectric property and possess minimal defect. A large open circuit voltage of about 1.0 V was observed and an increase in current by three orders in magnitude is obtained under UV illumination. The enhanced photovoltaic response observed in the present work is due to the twin contribution of novel design of photovoltaic cell having embedded IDEs and growth of good quality PZT film giving an enhanced ferroelectric photovoltaic effect.

Acknowledgments

The authors acknowledge the financial support from the Department of Science and Technology, Government of India to carry out this work. The authors are thankful to the University of Delhi for providing financial support and experimental facilities to carry out this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mssp.2019.104723.

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