Enhanced Photocurrent in Transparent Lead Zirconate-Titanate Thin Film Capacitors Under Sun Light Illumination

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ABSTRACT

$(Pb)(Zr_{0.52}Ti_{0.48})O_3$ films were fabricated on $LaNiO_3$ (LNO)/ In_2O_3 90%$SnO_2$10% (ITO) layered transparent electrodes on glass substrates, using chemical solution deposition. The electrical and optical properties of transparent ITO/LNO/PZT/LNO/ITO capacitors fabricated on glass substrates were studied. The remnant polarization (P_r) of the transparent ITO/LNO/PZT/LNO/ITO/glass capacitors was determined from P-E hysteresis loops measurements. Excellent optical transmittance was observed for the whole capacitor structure. The importance of a high performance transparent capacitor is that this structure may enable a new generation of high efficiency transparent electronic devices such as solar energy storage, photovoltaic, and intelligent windows, among others.

INTRODUCTION

$(Pb)(Zr_{0.52}Ti_{0.48})O_3$ [PZT] is being extensively researched due to its large field of applications in different devices such as non-volatile ferroelectric random access memories (FeRAMs), transducers, sensors and actuators [1-3]. It is also being studied for applications to nanofluidic and photovoltaic devices [4-6]. High performance transparent capacitors may enable a new generation of transparent electronic devices such as high-efficiency solar energy storage and photovoltaic devices, and intelligent windows.

Considerable efforts have been undertaken to grow highly transparent PZT films on glass substrates using indium tin oxide (ITO) layers as bottom electrodes [7-9]. ITO has very low electrical resistivity, high infrared reflectivity, and high UV absorption, which makes it an excellent transparent bottom electrode [10]. At room temperature, ITO has a cubic structure with lattice parameter a = 1.022 nm. This is almost two and half times bigger than that of PZT (a ~ 0.404 nm), producing a large lattice mismatch between PZT and ITO [10, 11].

Conductive metallic electrodes such as $SrRuO_3$ (SRO) and $LaNiO_3$ (LNO) have been studied for growing PZT films with good crystalline textures and excellent polarization [12, 13]. The oxide electrodes have also been reported to reduce fatigue and reduce leakage current density [13]. LNO, like PZT, has a perovskite pseudo cubic structure with a lattice parameter of 0.386 nm, which is close to that of PZT (0.404 nm) [11]. Studies performed on the LNO vs ITO electrode layer indicate that the thickness of the LNO layer on a glass substrate must exceed 200 nm in order to achieve good electrical conductivity. However, a 200 nm thick LNO layer is non-transparent. On the other hand, ITO layers are highly transparent even when they are relatively thick. PZT films grown directly on ITO layers are highly transparent, but exhibit low crystallinity and preferential orientation, in large extent due to the large lattice miss match between PZT and ITO, resulting in low remnant polarization. The solution is then to use a thin transparent layer of LNO as a buffer layer between PZT and ITO.

This paper focuses on a report of the optical and electrical properties of transparent PZT capacitors with layered LNO/ITO electrodes on glass substrates using a chemical solution deposition (CSD) technique. Structural data on these capacitors has been published elsewhere [6].

EXPERIMENTAL

The solution for the growth of LNO films was prepared using lanthanum nitrate hexahydrate (Strem 99.999%) and nickel acetate tetrahydrate (Aldric 99.998%) as precursor materials along with 2-methoxyethanol [2MOE] (Aldric 99.9 %) as a solvent. The powders were dissolved in the solvent by heating and stirring in a flask. The solution was then transferred to a container using a 0.2µm filter. Commercially available ITO coated glass from Delta Technologies (1” x 1” with thickness 200 nm) was used as a substrate. Prior to deposition of LNO, the glass substrates were cleaned with acetone and methanol. The LNO layer (40 nm thick) was deposited by spin coating at a speed of 3000 rpm for 30 seconds. The wet film was pyrolized immediately in air at 450^{o}C for 15 min and final crystallization of the pyrolized film was achieved by annealing in air at 650^{o}C for 20 min.

The PZT solution was prepared using lead (II) acetate trihydrate (Aldric 99%), zirconium (IV) propoxide (Aldrich 97%) and titanium (IV) isopropoxide (Aldric 99.9 %) as precursor materials and 2MOE as a solvent. The molar ratio Zr/Ti was kept at 52/48 and 20% excess Pb was used to compensate for the loss of Pb from the film due to volatile PbO during annealing. The zirconium (IV) propoxide powder was mixed with 2MOE in a flask by stirring. The titanium (IV) isopropoxide was then added to the above solution and stirred. Finally, the lead (II) acetate trihydrate was dissolved into the Zr/Ti solution by heating at 100°C for 1 hr coupled with stirring. PZT layers (90 nm thick) were then grown on the LNO/ ITO coated glass substrate at a speed of 3000 rpm for 30 seconds. The wet film was pyrolized by heating in air at 450°C for 5 min and then crystallized by annealing at 650°C for 20 min in air. A photograph of the final product and a schematic of the multilayer heterostructure are shown in Figure 1 and 2 respectively.

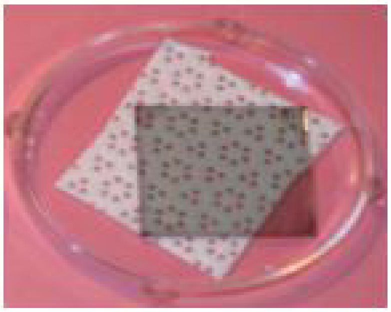

Figure 1. Photograph of a glass substrate coated with the transparent capacitor heterostructure.

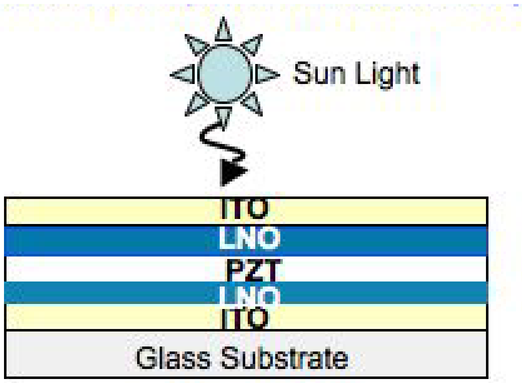

Figure 2. Schematic illustrating transparent capacitor heterostructure components.

The optical transmittance of the PZT films was measured using a double-beam UV/Vis spectrophotometer (Perkin Elmer Lambda 950).

For initial characterization of the ferroelectric properties of the PZT capacitors, transparent ITO/LNO electrodes were deposited on PZT, with the help of a shadow mask using a DC magnetron sputter-deposition system (AJA international). The typical thickness of the ITO/LNO electrodes was 280 nm, respectively and was measured, using a surface profilometer (Tencor, Alphastep 500). The diameter of the ITO/LNO electrodes for electrical characterization was 300 μm. The hysteresis loop for the PZT-based capacitors was obtained using a Radiant Technology RT 6000HVA high voltage measurement system and the dissipation factor (tan δ) of the film was measured at 10 kHz using a Hewlett Packard HP4192A low frequency analyzer.

DISCUSSION

Optical transmittance data for glass, ITO/glass, LNO/ITO/glass, PZT/LNO/ITO/glass and LNO/PZT/LNO/ITO/glass is shown in Figure 3. The LNO/PZT/LNO/ITO/glass structure exhibits 75% to 80% transmittance, within the visible light range, which is close to the transmittance of ITO/Glass. More importantly, the transmission of the LNO/PZT/LNO/ITO/glass structure retains better than 75% transparency all the way up to about 2800 nm wavelength light. This property is relevant to solar cell and photovoltaic applications because it expands the available spectrum for integrating into light harvesting devices.

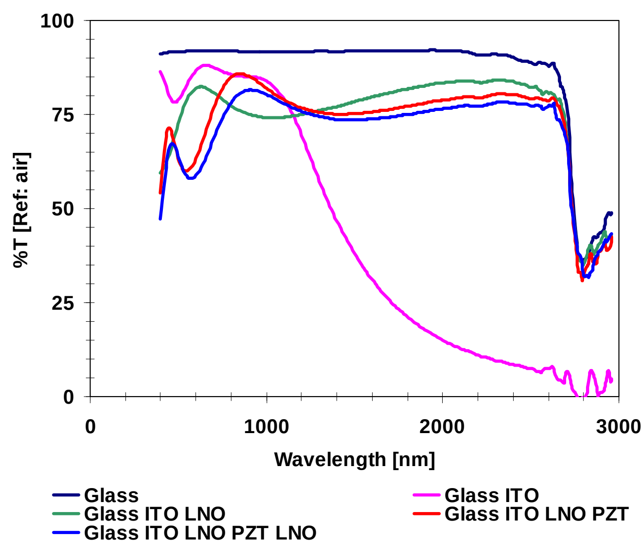

Figure 3. Transmission spectra of glass, ITO/glass, LNO/ITO/glass, PZT/LNO/ITO/glass and LNO/PZT/LNO/ITO/glass

Preliminary electrical data on these transparent capacitors indicate unusual interaction with UV light. The experiment involved the following steps. First, I vs V data was collected on a virgin capacitor with no UV light illumination, as indicated in Figure 4. Subsequently, I vs V data was collected with UV illumination and significantly more current was measured through the capacitor (insert in Fig. 4). The breakdown voltage is approximately 4 V. The magnitude of the current suggests that defects have been created in the capacitor structure, thus enabling the passage of electrons. After the first run, a second run was performed under similar conditions, as shown in Figure 5. In this case the current going through the capacitor with no UV light is much higher at smaller voltages and the capacitor shows now a resistive behavior upon UV illumination.

Clean Technology 2008, www.ct-si.org, ISBN 978-1-4200-8502-0

Fig. 6 shows hysteresis loops of the transparent PZT capacitor measured at 5 V, 7 V, 9V and 10 V. This capacitor exhibited P_r ~ 29 μC/cm^2 and dielectric loss of 0.04 (as shown in Fig. 7). The value of P_r for our transparent capacitor is close to that of reported in ref [8] for semi-transparent PZT capacitor and almost one-half of that of our semitransparent PZT capacitors. The lower P_r value can be attributed to the top electrode /PZT interface, and we are investigating this issue.

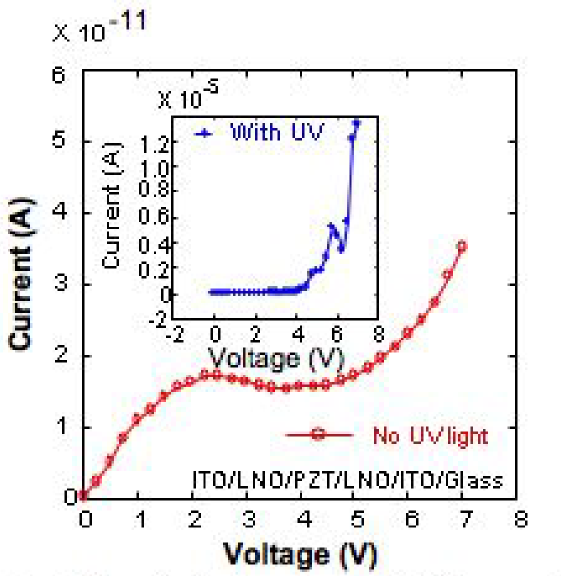

Figure. 4 I vs V for virgin transparent capacitor

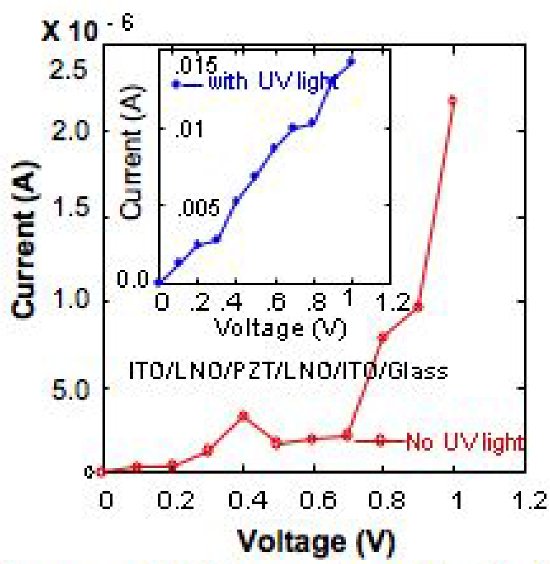

Figure. 5 I vs V for PZT transparent capacitor with defects created by sunlight illumination and voltage cycling.

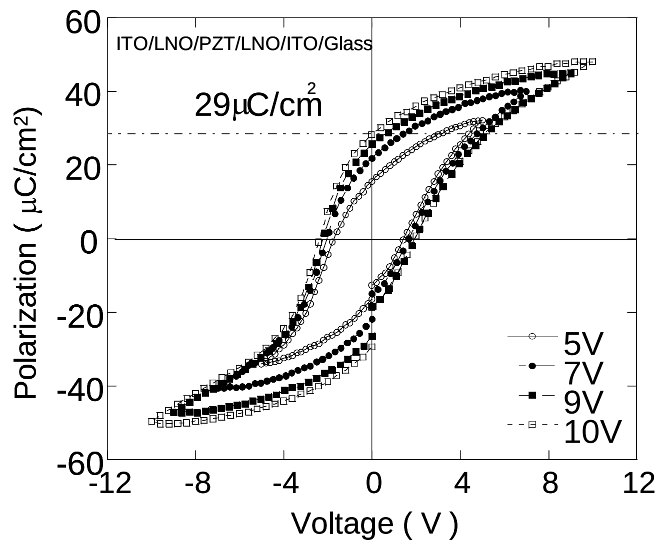

Figure. 6 P-E hysteresis loop for ITO/LNO/PZT/LNO/ITO capacitor on a glass substrate. The Voltage (V) = 0 shows P_r = 29 μC/cm^2.

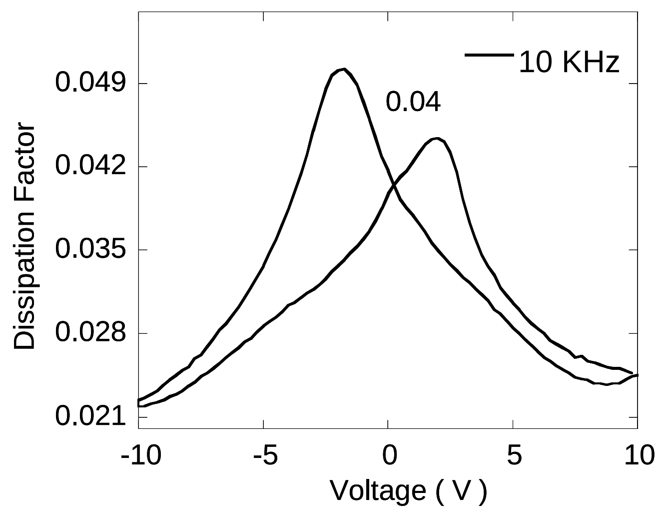

Figure. 7 Dissipation Factor (tan δ) for an ITO/LNO/PZT/LNO/ITO capacitor fabricated on a glass substrate.

CONCLUSION

Transparent ferroelectric PZT capacitors with relatively high remnant polarization (P_r) and low dielectric loss were synthesized on glass substrates using hybrid LNO/ITO heterostructure electrode layers. The hybrid ITO/LNO electrode approach provides a materials integration pathway to achieve transparent PZT-based capacitors with optical and ferroelectric response performance that can be controlled through a combined tailoring of the PZT/electrode interface and PZT composition and microstructure. This transparent capacitor can be used in a wide range of applications, including high-efficiency photovoltaic and solar energy storage devices, as well as smart coating for windows to control solar energy absorption, thus ambient temperature in buildings.

ACKNOWLEDGEMENTS

This work was supported by UChicago Argonne, LLC and the Department of Energy under Contract No. DE-AC02-06CH11357.

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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