Possible Origin of Photovoltaic Currents in Ferroelectric Pb-Based Perovskite Thin Films

Sandwip K. Dey and Prasad Alluri
Chemical, Bio & Materials Engineering and The Centers for Solid State Science/Electronics Arizona State University, Tempe, AZ 85287-6006

ABSTRACT: Photovoltaic measurements were carried out on sol-gel derived Pb(Nb,Zr,Ti)O_3 thin films with various Zr/Ti ratios. A typical photocurrent response had a polarization dependent transient component and a polarization independent steady state component. The former showed both magnitude and direction dependence of the polarization. Space charge fields that cause band bending near the metal ferroelectric interface, are believed to be the origin of the polarization dependent transient current. The magnitude of the space charge field was estimated from the transient photocurrent data. Upon illumination of the capacitor, some of the initially generated photocarriers are trapped at defect sites in the space charge region with a consequent decrease in the band bending. Once the trapping sites are consumed, a steady state is achieved. The polarization independent steady state photocurrents are attributed to the asymmetric Schottky contacts.

1. INTRODUCTION AND BACKGROUND

When bulk ferroelectrics (single crystal or ceramic) are illuminated with radiation of wavelengths corresponding to their band gap energies, a steady state photocurrent proportional to the magnitude of the remanent polarization and incident light intensity is generated. The popular mechanisms of the observed anomalous photovoltaic effect in single crystal and ceramics (1,2) are significantly different from the present observations on and proposed mechanism in thin films.

This paper presents and briefly discusses results of recent photovoltaic studies on ferroelectric PZT thin films. Based on the photoabsorption and photovoltaic experimental results, the possible origin of the complete photocurrent response is proposed.

2. EXPERIMENTAL

Ferroelectric lead zirconate titanate thin films (or PZT) of varying Zr/Ti ratios and thicknesses were deposited on Pt (111)/Ti/SiO_2/Si (100) substrates using an alkoxide sol-gel process. Semitransparent platinum top electrodes (~100 Å thick) were patterned using lift-off photolithography and sputtering techniques.

A schematic of the experimental set up for measuring the photovoltaic current is shown in Figure 1. Initially, a dc pulse of approximately 100 msec width and an amplitude of ±4 Volts or ±10 Volts was used to polarize the capacitors. The experiments involved illumination of UV light on poled 300 µm x 300 µm area ferroelectric capacitors and measuring the photocurrents generated. The UV light source was a mercury arc lamp with wavelengths ranging from 300 nm to 600 nm and having an intensity maximum at 365 nm.
wavelengths ranging from 300 nm to 600 nm and having an intensity maximum at 365 nm. No filter was used during the experimentation. The source was connected to a controller to adjust the duration of illumination. A light pipe from the source illuminated the capacitor. The distance of the light pipe was fixed so that the intensity near the electrode was approximately 100 mW/cm². The top and bottom electrodes were connected across a resistor of 100 kΩ. To measure the current generated, a Tektronix 2440 Oscilloscope along with an amplifier of gain 1000 were used. In order to study the effect of short illuminations, a variable frequency chopper was necessary.

![Figure 1: Schematic experimental setup for photovoltaic measurements.](image)

Photoabsorption spectrometry experiments were conducted on PZT thin films deposited on sapphire. The absorption spectrum of PZT was obtained by the subtraction of sapphire absorption from that of PZT on sapphire absorption data.

3. RESULTS AND DISCUSSION

A typical photocurrent response had a polarization dependent transient component and a polarization independent steady state component. The former showed both magnitude and direction dependence of the polarization. Figures 2 (A) and (B) illustrates the transient photocurrent responses obtained from a Pb Zr$_{0.52}$Ti$_{0.48}$O$_3$ (or PZT 52/48, 5% excess PbO, 2000Å thick) thin film, after having being poled at +10 and -10 Volts, respectively. Transient photocurrent responses were also obtained from an identical thin film with prepoling voltages of ±4 Volts. The magnitude of the peak transient photocurrent increased with the poling voltage. Similar results were observed on other compositions, namely 52/48 (with 10 and 15% excess PbO), 60/40 (with 15% excess PbO) and 40/60 (with 15% excess PbO). It was observed that the peak of the transient and the shape depended on the composition of the thin film. For some compositions (e.g. 2% Nb doped
Figure 2: Transient photocurrent response of PZT thin film poled at (a)+10 V, (b) -10 V.

Scale: horizontal: 1 cm = 50 ms  vertical: 1 cm = 81.6 μA/cm²

The steady state photoresponses of PZT (52/48 with 5% excess PbO) thin film capacitors were independent of the direction and magnitude of the poling voltage (and therefore of the polarization). The sign and magnitude of the steady state photocurrent for capacitors poled at ±4 and ±10 Volts were all identical.

Figure 3 is a plot of $\alpha^2$ ($\alpha$ is the absorption coefficient) versus photon energy, E. The band gap energy ($E_g$) was obtained by fitting a straight line in the high energy regime of the spectrum and extrapolating to $\alpha^2 = 0$. The absorption distance (which is the inverse of $\alpha$) was estimated to be 2000 Å for a wavelength (330 nm) corresponding to the band gap energy (~3.56 eV). Note that for lower wavelengths (i.e., for $E > E_g$), absorption distances are shorter. Thus, the absorption distances for the PZT thin films were assumed to be less than 200 Å.

Figure 3: Photoabsorption spectrum obtained on a 0.5 mm PZT thin film

Space charge fields that cause bend bending near the metal ferroelectric interface, are believed to be the origin of the polarization dependent transient photocurrent. For
instance, at time $t=t_0$, when a negatively poled capacitor is illuminated, the time-dependent space charge potential may be represented by Figure 4. Note the trapping of electrons at the positively charged trapping sites and the initiation of the negative transient photocurrent. The end of the transient occurs at $t>t_2$, i.e., at the moment the trap sites (represented by circles and distributed in energy) are completely full and therefore, neutral. Thus, the transient could only be observed after repoling. Since the top interface dictates the magnitude of transient photocurrent, the asymmetry in the band bending at the top interface for both the positive and negative poling voltages is reflected in the asymmetry of the transient photocurrent. From the transient photocurrent, the magnitude of the space charge field was estimated to be approximately 200 kV/cm. Further illumination gives rise to the Schottky barrier dominated steady state photocurrent only.

**Figure 4:** Band diagram of a negatively poled capacitor, during illumination.

**References:**


(2) P.S. Brody and F. Crowne, ibid, 4 p955 (1975).

**Acknowledgement:** President's Fund, California Institute of Technology, U.S.A.