Slow relaxation of piezoelectric response in CdZnTe ferroelectric semiconductor single crystals

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The piezoelectric response in Cd$_{0.9}$Zn$_{0.1}$Te (CZT) semiconductor single crystals has been investigated by analyzing room temperature impedance spectra. The polarization is significantly influenced by light illumination. A slow relaxation process of the piezoelectric response has been observed with a relaxation time of 37 s, which is comparable to the discharge current results. The frequencies for piezoelectric resonance and antiresonance can be tuned to lower values when a bias field is applied and can be recovered when the bias field is removed. These phenomena may be universal for ferroelectric semiconductors and can be explained by a slow relaxation model in dielectrics. © 2007 American Institute of Physics. [DOI: 10.1063/1.2799259]

It has been demonstrated that off-center site occupancy in semiconductor alloys may lead to a ferroelectric behavior, which results from the large size mismatch between the ionic radii of Zn and Cd. The I–VI compound semiconductor Cd$_{1-x}$Zn$_x$Te (CZT) was thereafter identified to be ferroelectric by Weil et al. The ferroelectricity in these binary mixed crystals is due to the large size mismatch between the ionic radii of Zn and Cd (Cd$^{2+}$=0.103 nm, Zn$^{2+}$=0.083 nm). An electric dipole is built up when a Zn ion occupies an off-center site along the ⟨111⟩ direction, similar to the case of lead zirconate titanate with a rhombohedral structure. Recently, CZT has received considerable attention because of its potential application in high resolution room temperature gamma radiation spectroscopy. Attempts have also been made to use CZT for nonvolatile memory device applications due to its ferroelectricity and good match of lattice parameters with silicon. Writing and reading processes can be conducted on CZT wafers.

It is well known that all ferroelectrics show piezoelectricity. This characteristic provides us an alternative way to characterize CZT for electronic applications. For instance, we can probe the piezoelectric response of CZT under a dc bias field. As pointed out by Li et al., an applied electric field will induce both a rapid effect and a slow effect in dielectrics. A slow relaxation of field-induced piezoelectric resonance in paraelectric barium stannate titanate (BaTi$_{0.8}$Sn$_{0.2}$O$_3$) ceramics has already been found. In this letter, we report the piezoelectric response in Cd$_{0.9}$Zn$_{0.1}$Te ferroelectric single crystal. A slow relaxation process was observed under an applied dc bias field. Discharging current was measured as a function of time to understand the slow relaxation process. The results show that the influence of the slow effect cannot be ignored in the application of II–VI type ferroelectric semiconductors especially when a bias electric field is applied.

Cd$_{0.9}$Zn$_{0.1}$Te ingot was grown with a modified Bridgman method. High-purity (99.999 99% for all) raw materials of Cd, Zn, and Te were used to reduce the unintended impurities. In order to reduce the bulk conductivity, 30 ppm indium was introduced. The ingot was cut along ⟨111⟩ surface with a dimension of 10×10×2 mm$^3$. Gold electrodes with a diameter of 5 mm and a thickness of about 60 nm were deposited by thermal evaporation onto the ⟨111⟩ surfaces which had been mechanically and chemically polished. A precision impedance analyzer (Agilent 4294A) was used to measure the dielectric and piezoelectric responses of the samples under dc bias field. For the transient current measurement (I–t), a high resistance meter (Agilent 4339B) was employed.

Figure 1 shows the room temperature impedance spectra of a CZT single crystal near the piezoelectric resonance frequency measured in complete darkness and under room light illumination, respectively. The frequency range is 5.14–5.16 MHz and the applied ac signal level is 0.5 V. For convenience, we assign $f_r$ and $f_a$ as the resonance and antiresonance frequencies corresponding to the minimum impedance $Z_r$ and maximum impedance $Z_a$, respectively. As shown in Fig. 1, $f_r$ and $f_a$ of the samples are 5.1513 and 5.1519 MHz, respectively. The light illumination on the sample has no influence on the resonance and antiresonance frequencies. However, it results in reduced impedance, indi-
cating the influence of nonequilibrium carriers on the conduc-
tivity. Under light illumination, photogenerated carriers
accumulate at the semiconductor-metal interface and narrow
the depletion layer. The light illumination also results in in-
creased polarization due to the same reason as reported in the
literature.5

By applying and then removing a dc bias voltage, a se-
ries of interesting phenomena can be observed after repeated
measurements, as shown in Fig. 2. The numbers 1–10 in Fig.
2(a) indicate the sequence of measurement. The time be-
tween each consecutive measurement is about 7–10 s. When
a bias voltage of 20 V is applied, both \( f_r \) and \( f_a \) keep on
shifting to lower frequencies even after the tenth measure-
ment, while at the same time, both \( Z_r \) and \( Z_a \) change only
slightly. The resonance and antiresonance frequencies gradu-
ally return to their original values when the bias is removed.
Similar results can be detected even when no light is illumi-
nated on the sample. In general, the resonance frequency
depends on the geometry and piezoelectricity of the materi-
als. It is well known that the change of sample size due to
converse piezoelectric effect is almost instantaneous. There-
fore, the observed phenomena cannot be explained by con-
verse piezoelectric effect under a bias field. Obviously, this
relaxation phenomenon has intrinsic correlation with slow
polarization effect. Slow effect is always caused by the
movements of space charges or relaxation of locally bound
dipoles.6

\[
\frac{Q(t)}{Q(0)} = 1 - r \exp\left(-\frac{t}{\tau}\right),
\]

where \( Q(t) \) is any relaxation parameter and \( \tau \) is the charac-
teristic response time. In our experiment, \( f_i \) is regarded as the
relaxation parameter. So we have \( Q(0) = f_0 \) and \( Q(t) - Q(0) = f \). Equation (2) can then be rewritten as

\[
\ln f = \ln(-rf_0) - \frac{t}{\tau}.
\]

The characteristic relaxation time \( \tau \) can be obtained by
calculating the slope of \( \ln f \) versus \( t \). Taking the relaxation
process when the bias field was removed as an example, Fig.
3 shows the relationship between \( \ln f \) versus \( t \) at room tem-
perature. A linear time dependence of \( \ln f \) can be clearly
identified. The calculated relaxation time \( \tau \) from the slope of
the best fit line, as shown in Fig. 3, is 37 s. This relaxation
time is almost the same as the one measured in the dark. It
implies that photogenerated carriers have no influence on the
slow effect.

Although a relaxation time of about 37 s was determined
in CZT single crystal, its microscopic origin is still not clear.
Such a relaxation process is definitely not a result of a con-
verse piezoelectric effect nor of the movement of free carri-
ers under a bias field since both of the two effects have
response time usually below a few microseconds. Possible
origin of this slow relaxation, as suggested by Li et al.,5
could be the locally bound dipoles, space charges, or homo-
charges injected from the electrode into the crystal under a
bias field. The transient current after the removal of the bias
voltage of 20 V was measured and shown in Fig. 4. The
discharging current of the CZT crystal roughly exhibits a
straight line in a double logarithmic plot of the current and
Hargen’s universal dielectric relaxation law in solids.9 In the

FIG. 1. Impedance spectra of CdZnTe measured in the dark (closed circle)
and under room light (open circle).

FIG. 2. Impedance spectra of CdZnTe measured under room light when a
bias voltage of 20 V was applied (a) and removed afterwards (b). The di-
rection of arrows and the corresponding numbers (1–10 and 1–11) indicate
the sequence of measurement (at room temperature). The time between each
consecutive measurement is about 7–10 s.

FIG. 3. In \( f \) vs time at room temperature when the bias voltage of 20 V was
removed. The open circles are experimental data and the solid line is best fit
line according to Eq. (3).

To investigate this slow relaxation process, we define para-
meter \( f \) as,

\[
f = f_i - f_0, \quad i = 1, 2, \ldots, 11,
\]

where \( f_i \) is the resonance or antiresonance frequency in the
ith measurement and \( f_0 \) is the resonance or antiresonance
frequency measured without any bias field. Li et al. proposed
an equation to describe a random relaxation process in di-

\[
Q(t) = \frac{Q(0)}{1 - \frac{Q(0)}{f_0}} \left(1 - \exp\left(-\frac{t}{\tau}\right)\right).
\]
time domain relaxation studies, if we plot a graph of the current multiplied by time as a function of time, the location where a local maximum is found corresponds to the intrinsic relaxation time. As shown in Fig. 4, two local maxima (A and B) can be found at the times of 45 and 68 s, respectively, which suggest the existence of two relaxation processes with relaxation times of 45 and 68 s, respectively. The relaxation time obtained is somewhat larger than the one obtained from Eq. (3), where only one relaxation process was taken into consideration and therefore resulted in shorter relaxation time. Furthermore, a maximum at C corresponding to a relaxation time of 310 s can be observed in Fig. 4. Such a long time relaxation process did not contribute too much to the field induced changes of the resonance or antiresonance frequencies since our total experiment time is less than 90 s, as shown in Fig. 3.

The similar relaxation time obtained from both the field-induced change of piezoelectric response and the depolarization current indicates that the slow effect can be originated from the injection and decay of homocharges in the dielectrics. When the bias field is applied, the injected homocharges gradually build up bound dipoles in the surface of the dielectrics with a direction antiparallel to the bias field. Due to the interaction of surface bound dipoles and the spontaneous polarization, the piezoelectric resonance can be retarded and shift to lower frequencies gradually. When the bias field is removed, the homocharges on the top and bottom surfaces are gradually neutralized and the surface bound dipoles are reduced. Therefore, the piezoelectric resonance frequencies gradually return to their original values. A similar slow effect has also been observed in paraelectric barium stannate titanate with a relaxation time of 71 s near room temperature.7

In summary, the impedance spectra and depolarization current of CZT ferroelectric semiconductor single crystal samples were investigated. Analysis of the impedance spectra showed that the piezoelectric resonance frequency of CdZnTe is significantly influenced by an applied bias field. The effect of slow relaxation of the surface bound dipoles should not be ignored for practical device applications whenever a bias voltage is applied.

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6J. D. Li, H. Shen, and M. Chen, Theories of Dielectrics (Chinese Science, Beijing, 2003) [in Chinese].