

Ferroelectric origin in one-dimensional undoped ZnO towards high electromechanical response[†]

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SUPPORTING INFORMATION

1 Seed layer

The 30 nm ZnO seed layer was sputtered on Pt/Si substrate. Table 1 shows the process parameters for ZnO seed layer preparation.

Table 1: *Process parameters in ZnO seed layer preparation*

Parameters	
RF power	100 watt
Chamber pressure	4.5x 10 ⁻² mbar
Argon flow	25 sccm
Substrate to target distance	5 cm
Deposition time	4 minutes
Thickness	30 nm

2 Polarization-electric field loop (P-E loop)

We have used a modified Sawyer Tower circuit and a digital oscilloscope display (TDS1000-EDU, Tektronix, Canada, US) to verify ferroelectric property of the samples. Schematic of modified Sawyer Tower circuit [1, 2] used in our experiment is presented in Fig. 1. Using this, ferroelectric material is characterized under AC electric field. In conventional Sawyer Tower circuit current through the sample under test consists of polarization current, leakage current and stray capacitance. Presence of stray current distorts the P-E hysteresis loop whereas presence of leakage current does not give a closed hysteresis loop. In this experiment, the Sawyer Tower circuit is modified by adding two network blocks to reduce the effect of leakage current and stray current on polarization current. These two network blocks are a current booster network and a phase shifter network. Fig. 1 shows these two network blocks and their detailed circuitry (below). The current booster network amplifies the input current signal. It consists of two stages; a voltage unity gain inverting operational-amplifier (op-amp) circuit and a NPN-PNP transistor current amplifier circuit. The voltage inverter inverts input voltage signal at the op-amp output terminal without changing its amplitude whereas the current amplifier amplifies input current signal from the op-amp output terminal. Output current signal from the amplifier stage is fed to the phase shifter network block. This block consists of six sub-blocks of resistor-capacitor (R-C) networks in series where in each sub-block resistor and capacitor are connected in parallel to each other (Fig. 1). Each of the R-C network shifts input current signal (out of the NPN-PNP network) phase by 30° . So, the total phase shifter block shifts input current signal phase by 180° . When this phase shifted current signal (-stray current and -leakage current) is added to the output current signal of the sample (polarization current+stray current+leakage current) under test, effect of stray current and leakage current on polarization current gets reduced.

Here, a function generator (F) generates AC voltage signal V_{app} . The voltage is fed to the current booster block to have sufficient current (for amplifying current signal) to drive the load. Output signal from current booster network is divided into three parts; one of them (drawing major portion of the current signal) is fed to the ferroelectric capacitor (C_f) under investigation whereas other two are fed to the phase shifter network and the voltage attenuating network respectively. Voltage (V_0) across a reference capacitor (C_0 , generally with higher capacitance value

than C_f) which is in series with C_f is recorded and displayed in digital oscilloscope. X-axis of the display denotes attenuated applied AC voltage obtained from attenuator network (which contains mainly voltage divider) and Y-axis gives corresponding change in V_0 as well as the charge in C_0 . As C_0 and C_f are in series, charge stored in both the capacitors will be the same (i.e., $Q_f=C_fV_f=Q_0=C_0V_0$, $V_f > V_0$ as $C_0 > C_f$). So, the Y-axis will give charge as well as polarization behavior in C_f with respect to the attenuated applied AC (or electric field). Theoretically, as C_0 has larger capacitance than C_f , the voltage V_0 across it will be very small with respect to V_f . So, V_f will be almost equal to V_{app} . Thus, V_{app} gives the electric field inside C_f . Different values of capacitor starting from 10 nF to 1 μ F are selected as C_0 by switch 2 (SW2). To reduce the effect of stray capacitance and leakage current on polarization, a compensation network has been introduced in Sawyer Tower circuit. Inverting operational amplifier in this network inverts V_{app} and in the next stage R-C (R_2 - C_1) network generates reverse phase stray current and leakage current. Integration of these at C_f and C_0 junction gives only the effect of polarization current in the output terminal. R_2 and C_1 values used in this experiment are varied from 10 M Ω to 1 K Ω and 10 nF to 1 μ F, respectively. A selector (SW1) was used to select combinations of R_2 and C_1 . The op-amp buffer network provides high impedance match in between the output terminal and display. Table 2, 3 and 4 have detailed about the necessary electronic components that were used in the modified Sawyer Tower circuit. The derived electronic component values mentioned here are calculated using the equations for current booster phase shifter network as shown in Fig. 1. Fig. 2 demonstrates the experimental setup of modified Sawyer Tower circuit along with oscilloscope display, used here for ferroelectric characterization. So, the Sawyer Tower circuit gives information about the polarization of ferroelectric material with respect to the electric field in it. Electric polarization with respect to electric field (P-E characterization [3]) gives different patterns for different electrical elements. For ideal linear capacitor, it gives a straight line (Fig. 3 i) while for an ideal resistor it gives a homogeneous oval (Fig. 3 ii). In case of a practical capacitor, resistive loss is always present, so the P-E response looks like a tilted oval (Fig. 3 iii). For an ideal ferroelectric material, nonlinear hysteresis can be observed in P-E response loop (Fig. 3 iv).

Table 2: *Parameters for function generator*

Input voltage	Signal frequency	Coupling capacitor	Impedance $Z_c = 1/(2\pi f C_c)$
V	Hz	μ F	Ω
5.5 V_{P-P}	400	30	130.8

Table 3: *Parameters for current booster network*

R_1	R_4	R_5	R_{bn}	R_{cn}	R_{en}	R_{bp}	R_{cp}	R_{ep}
K Ω	K Ω	K Ω	K Ω	K Ω	K Ω	K Ω	K Ω	K Ω
10	2	1	42	0.5	0.5	42	0.5	0.5

Table 4: *Parameters for phase shifter, attenuator and reference capacitor network*

R_2	C_1	R_7	R_3	C_0
M Ω	pF	M Ω	M Ω	nF
1	220	10	1	8.33

As the structure of interest is single crystalline, wurtzite (vertically aligned in-situ sample), the focus will be on this structure only. In a wurtzite [001] directional single crystalline ferroelectric material (having space group $P6_3mc$), [001] is a possible orientation, [4] where permanent dipole moments lie. Dipole moments lying (parallel or antiparallel with each other) in [001] direction create domains with respect to each other. In a single domain, all the dipole moments have same orientation. The parallel or nearly parallel domains with respect to the applied electric field need low energy to get aligned with the electric field. Whereas, domains with 180° alignment with the applied field need more energy for alignment. From the ideal ferroelectric P-E loop in Fig. 3 iv, this can be observed i.e., initial application of electric field arranges the nearly parallel domain walls or boundaries. Increasing electric field arranges the 180° domains, before reaching to a saturation state. The polarization value at saturation is extrapolated to y-axis to give spontaneous polarization value. From saturation, when the electric field is reversed the polarization does not follow the previous path, rather it maintains the saturation polarization value upto the zero applied field. High negative applied field is needed to bring down this polarization value to zero. Further increase in negative electric field, increases polarization in negative direction until the negative polarization reaches to satura-

tion. Again increment of electric field towards positive direction, holds the negative saturation polarization until electric field becomes zero. High positive electric field is required to nullify this negative polarization. The electric field values which bring down the positive and negative polarization to zero are called coercive field ($\pm E_c$). The remaining polarization in the material at zero electric field is called remnant polarization. Ideally remnant polarization and spontaneous polarization have same values. Spontaneous polarization is related to electric field by,

$$D = P_s + \varepsilon_0 \varepsilon_r E \quad (1)$$

where D is the electric displacement (C/m^2), ε_0 is the dielectric permittivity of free space (F/m), ε_r is the relative dielectric permittivity (F/m), E is the applied electric field (V/m) and P_s is the spontaneous polarization (C/m^2). When electric field is zero, $D=P_s$. So, in a single domain ferroelectric material at zero electric field D has two values either positive or negative depending upon the direction of spontaneous polarization and in a multi-domain ferroelectric material D lies in between these positive and negative spontaneous polarization values. From P-E loop of ferroelectric material, spontaneous polarization and applied electric field is given by:

$$P_s = Q/A = (C_0 V_0)/A \quad (2)$$

$$E = V_{app}/d_a \quad (3)$$

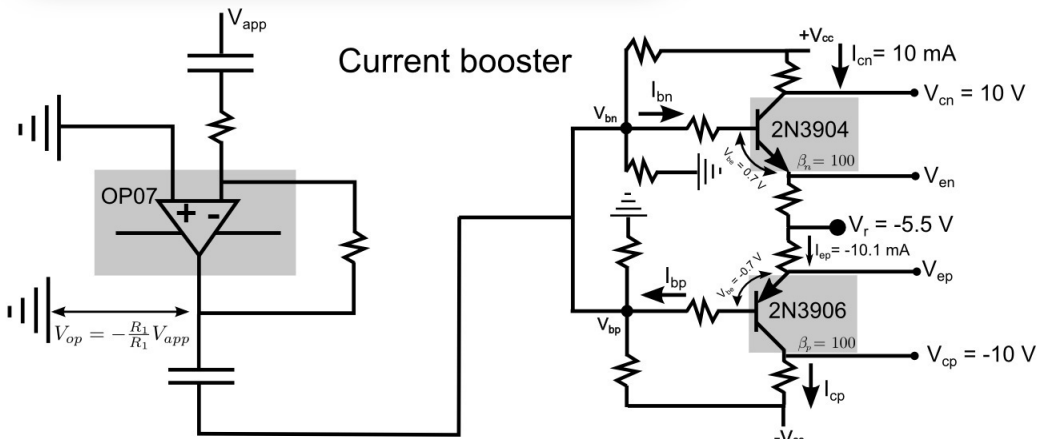
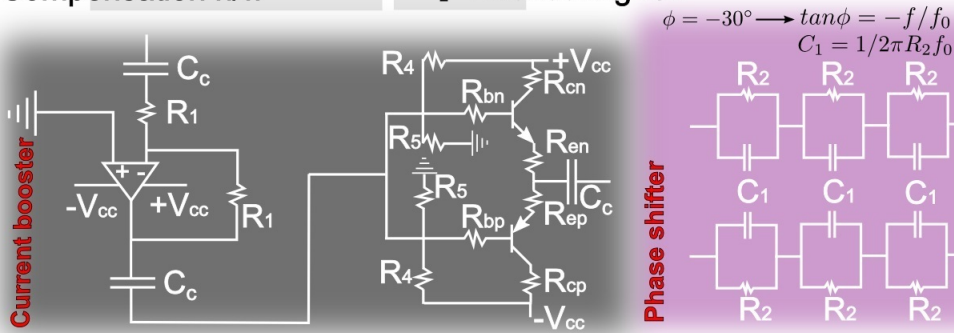
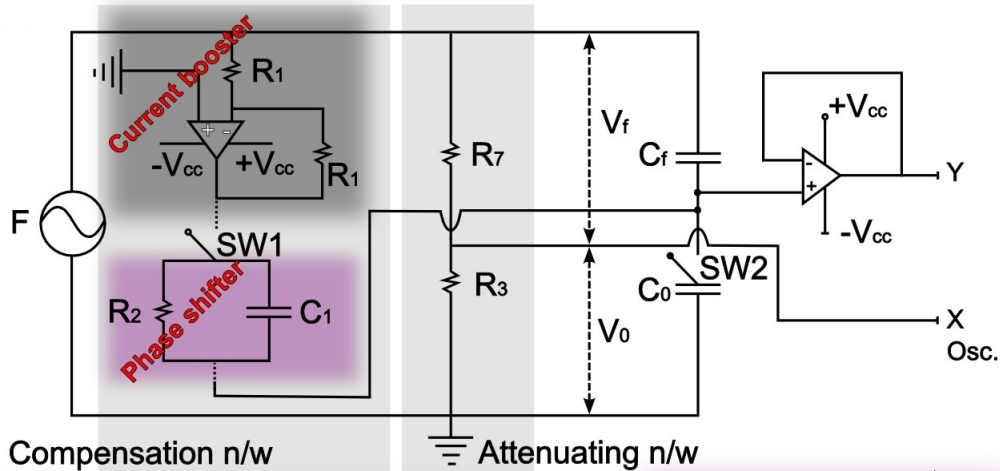
where A is the area (m^2) and d_a is the thickness (m) of the ferroelectric material. Remnant polarization and applied electric field of this sample is determined using equation 2 and equation 3. Here, $A = \pi(250\mu m/2)^2$. In ZnO nanorod sample, the C_0 value used in modified Sawyer Tower circuit was 8.33 nF and output voltage across C_0 was 0.5 volt (as observed from oscilloscope).

3 SEM of ZnO nanorod cross-section

SEM image of a single ZnO nanorod cross-section is shown in Fig. 4. This ZnO nanorod has hexagonal cross-section which is 50 nm in diameter. Schematic of this hexagonal cross-section shows [100] and [110] directions considering three lattice vectors a_1 , a_2 and a_3 in hexagonal wurtzite structure.

References

- [1] Sawyer, C. B.; Tower, C. H. *Phys. Rev.* 1930, 35, 269.
- [2] Das, S. C.; Shahee, A.; Lalla, N. P.; Shripathi, T. *Proceedings of the 54th DAE Solid State Physics Symposium 2009*, 54, 439.
- [3] Damjanovic, D. *Rep. Prog. Phys.* 1998, 61, 1267.
- [4] Wood, C.; Jena, D. *Polarization Effects in Semiconductors: From Ab Initio Theory to Device Applications*; Springer, 2007.



For 2N3904

- $\frac{+V_{cc} - V_{cn}}{I_{cn}} = R_{cn}$
- $I_{en} = \frac{\beta_n + 1}{\beta_n} I_{cn}$
- $V_{en} = -V_{ben2} = V_{ben1} + V_T \ln\left(\frac{I_{cn1}}{I_{cn2}}\right)$
- $R_{en} = \frac{V_{cn} - V_r}{I_{en}}$
- $I_{bn} = I_{en} - I_{cn}$
- $V_{bn} = \frac{R_5}{R_5 + R_4} V_{cc}$
- $R_{bn} = \frac{V_{bn} - V_{ben2}}{I_{bn}}$

For 2N3906

- $V_{bp} = \frac{R_5}{R_5 + R_4} (-V_{cc})$
- $V_{ep} = -V_{bep} + V_{bp}$
- $I_{cp} = \frac{\beta_p}{\beta_p + 1} I_{ep}$
- $I_{cp} = I_{ep} - I_{bp}$
- $R_{bp} = \frac{V_{bp} - V_{bep2}}{I_{bp}}$
- $R_{cp} = \frac{(-V_{cc}) - V_{ep}}{I_{cp}}$

Figure 1: Shows schematic of the modified Sawyer Tower circuit along with circuit design details of the current booster and phase shifter. For the phase shifter, f_0 is the break frequency of each of the six R-C networks.

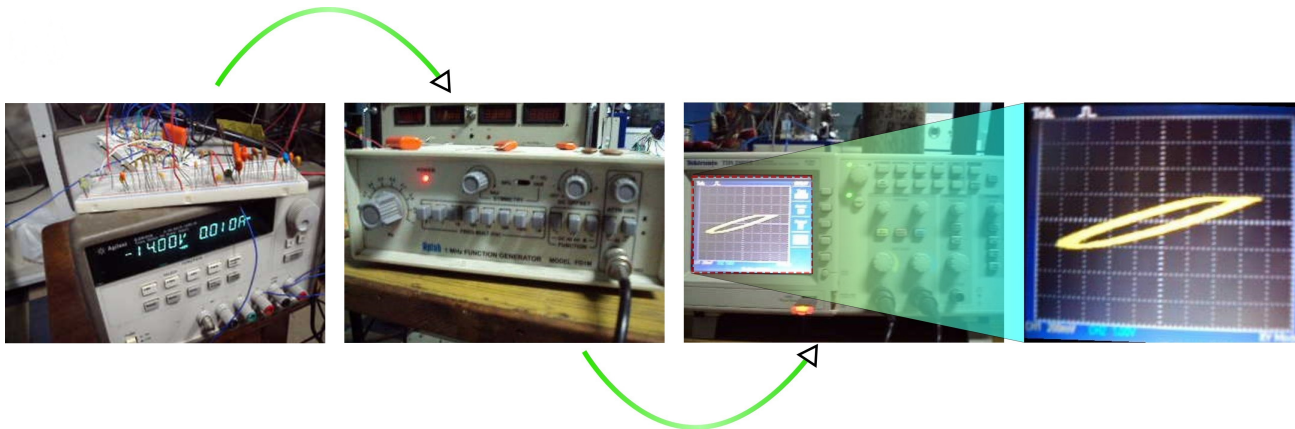


Figure 2: Experimental setup of modified Sawyer Tower circuit.

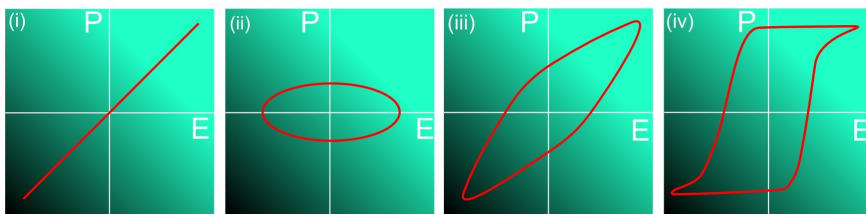


Figure 3: P-E loop of (i) an ideal capacitor, (ii) an ideal resistor, (iii) a lossy capacitor, (iv) an ideal ferroelectric material.

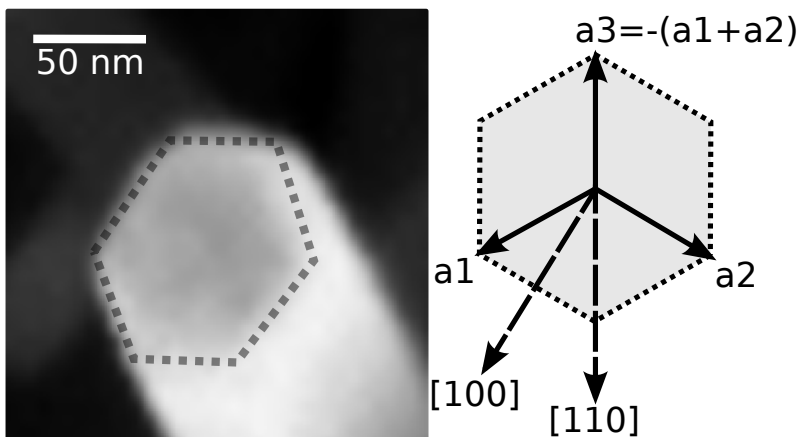


Figure 4: Shows SEM of a single ZnO nanorod with hexagonal cross-section.