Work function information of samples derived from KPFM

Three procedures are used to judge the characteristics of the PN junctions.

First is to determine the relationship of the work function for the four Au, Pt, BBPT and NBLT materials by measuring the contact potential difference between the four materials and probes. The specific judgment process is as follows.

When KPFM works, the electrostatic potential around the sample and probe is equal:

$$qV_{tip} - W_{tip} = qV_{sample} - W_{sample} \quad (1)$$

where V_{tip} and V_{sample} are the tip voltage and sample voltage, respectively. And W_{tip} and W_{sample} are the work function of tip and sample, respectively.

When two different samples are measured with the same probe and ground connection, the electrostatic potential relationship is as follows:

$$qV_{tip1} - W_{tip1} = qV_{sample1} - W_{sample1} \quad (2)$$

$$qV_{tip2} - W_{tip2} = qV_{sample2} - W_{sample2} \quad (3)$$

The sample1 and 2 represent two different samples. When two samples are on the same batch of substrates and are well grounded during measurement, the following relationship will be generated:

$$q(V_{cpd1} - V_{cpd2}) = W_{sample2} - W_{sample1} \quad (4)$$

where V_{cpd1} represent the contact potential difference between the tip and sample 1, respectively. Therefore, the order of magnitude of work functions for the samples and electrodes can be derived from the contact potential difference between the tip and sample V_{cpd}. By measuring, we have conform that $V_{cpdAu} > V_{cpdPt} > V_{cpdBBPT} > V_{cpdNBLT}$. Thus, the order of magnitude of the sample work function is $W_{NBLT} > W_{BBPT} > W_{Pt} > W_{Au}$.

Second is the judgement of the interface barrier height between materials and electrodes. For N-type and P-type semiconductors, the formulas for the barrier heights are $\Phi_B = W_M - \chi_S$ and $\Phi_B = E_g - (W_M - \chi_S)$, respectively. Therefore, the higher work function of electrode results in the higher the interface barrier height for N-type semiconductors and the lower the interface barrier height (worse leakage performance)

for P-type semiconductors.

At last, the conductive type can be accurately judged by combining the order of magnitude of work function information and the leakage information. As measured in the results, the leakage performance of Au/BBPT/Pt with asymmetric electrode are better than that of Au/BBPT/Au with symmetrical electrodes, and the leakage performance of Au/NBLT/Au with symmetrical electrodes is better than that of Au/NBLT/Pt. Therefore, we can determine exactly that BBPT is N-type and NBLT is P-type.

The derivation of formula (5)

The concentrations of majority carriers in N-region and P-region are N_e and N_h, respectively. The depletion region widths of in N-region and P-region are ω_p and ω_n, respectively. Then the charge density in the barrier region is as follows

$$\rho(x) = -qN_h \qquad (-\omega_p < \omega < 0) \qquad \text{(S1)}$$

$$\rho(x) = qN_e \qquad (0 < \omega < -\omega_n) \qquad \text{(S2)}$$

The depletion region width of PN junctions is as follows.

$$\omega = \omega_n + \omega_p \qquad \text{(S3)}$$

Because the entire semiconductor satisfies the condition of electrical neutrality, the total positive and negative charges in the depletion region are equal.

$$qN_h\omega_p = qN_e\omega_n = Q \qquad \text{(S4)}$$

Q is the amount of space charge accumulated per unit area on the depletion region. The poisson equation inside the barrier region of the abrupt junction is shown in the following formula.

$$\frac{d^2V_1(\omega)}{d\omega^2} = \frac{qN_h}{\varepsilon_h\varepsilon_0} \qquad (-\omega_p < \omega < 0) \qquad \text{(S5)}$$

$$\frac{d^2V_2(\omega)}{d\omega^2} = -\frac{qN_e}{\varepsilon_e\varepsilon_0} \qquad (0<\omega<-\omega_n) \qquad \text{(S6)}$$

Where, V_1(x) and V_2(x) are the potential in the negative and positive space charge region, respectively. Integrating above formula, the following formula will be given.

$$\frac{dV_1(\omega)}{d\omega} = \frac{qN_h}{\varepsilon_h\varepsilon_0} + C_1 \qquad (-\omega_p<\omega<0) \qquad \text{(S7)}$$

$$\frac{dV_2(\omega)}{d\omega} = -\frac{qN_e}{\varepsilon_e\varepsilon_0} + C_2 \qquad (0<\omega<\omega_n) \qquad \text{(S8)}$$

Where C_1 and C_2 are constants, which can be determined by boundary conditions. Since it is electrically neutral outside the barrier region and the electric field is concentrated in the barrier region, the boundary condition can be obtained as follows:

$$E(-\omega_p) = -\frac{dV_1(\omega)}{d\omega}\bigg|_{\omega=-\omega_p} = 0 \qquad \text{(S9)}$$

$$E(\omega_n) = -\frac{dV_2}{d\omega}\bigg|_{\omega=\omega_n} = 0 \qquad \text{(S10)}$$

According to (S7)-(S10), the following formula are obtained.

$$C_1 = \frac{qN_h\omega_p}{\varepsilon_h\varepsilon_0} \qquad \text{(S11)}$$

$$C_2 = \frac{qN_e\omega_n}{\varepsilon_e\varepsilon_0} \qquad \text{(S12)}$$

Since $N_h\omega_p=N_e\omega_n$ and $C_1=C_2$, the electric field in the barrier region can be expressed as the following formula.

$$E_1(\omega) = -\frac{dV_1(\omega)}{d\omega} = -\frac{qN_h(\omega+\omega_p)}{\varepsilon_h\varepsilon_0} \qquad (-\omega_p<\omega<0) \qquad \text{(S13)}$$

$$E_2(\omega) = -\frac{dV_2(\omega)}{d\omega} = \frac{qN_e(\omega+\omega_n)}{\varepsilon_e\varepsilon_0} \qquad (0<\omega<\omega_n) \qquad \text{(S14)}$$

Where, E_1 (ω) and E_2 (ω) are the electric field intensity in the negative and positive

space charge region, respectively. Integrating the formulas (S13) and (S14), it gets the potential in the barrier.

$$V_1(\omega) = (\frac{qN_h}{2\varepsilon_h\varepsilon_0})\omega^2 + (\frac{qN_h\omega_p}{\varepsilon_h\varepsilon_0})\omega + D_1 \quad (-\omega_p < \omega < 0) \qquad (S15)$$

$$V_2(\omega) = -(\frac{qNe}{2\varepsilon_e\varepsilon_0})\omega^2 + (\frac{qNe\omega_n}{\varepsilon_e\varepsilon_0})\omega + D_2 \quad (0 < \omega < \omega_n) \qquad (S16)$$

If the potential in the P-type neutral region is zero, the boundary condition under the thermal equilibrium condition is:

$$V_1(-\omega_p) = 0 \qquad V_2(\omega_n) = V_D \qquad (S17)$$

Substituting formula (S17) into formula (S15) and (S16) to get:

$$D_1 = \frac{qN_h\omega_p^2}{2\varepsilon_h\varepsilon_0} \qquad D_2 = V_D - \frac{qN_e\omega_n^2}{2\varepsilon_e\varepsilon_0} \qquad (S18)$$

Because the potential is 0 at ω=0, the potential is continuous everywhere, thus $V_1(0)$= $V_2(0)$. Put D_1 and D_2 into formula(S19) and (S20).

$$V_1(\omega) = (\frac{qN_h(\omega^2+\omega_p^2)}{2\varepsilon_h\varepsilon_0}) + (\frac{qN_h\omega_p\omega}{\varepsilon_h\varepsilon_0}) \quad (-\omega_p < \omega < 0) \qquad (S19)$$

$$V_2(\omega) = V_D - (\frac{qN_e(\omega^2+\omega_n^2)}{2\varepsilon_e\varepsilon_0}) + (\frac{qN_e\omega_n\omega}{\varepsilon_e\varepsilon_0}) \quad (0 < \omega < \omega_n) \qquad (S20)$$

Due to $V_1(0)$= $V_2(0)$, the depletion region width of PN junction can be estimated using following formulas:

$$V_D - (\frac{qN_e(\omega_n^2)}{2\varepsilon_e\varepsilon_0}) = (\frac{qN_h(\omega_p^2)}{2\varepsilon_e\varepsilon_0}) \qquad (S21)$$

When an electric field applied, an expression for the width of the depletion region is obtained.

$$\omega_{PN} = \sqrt{\frac{2\varepsilon_0\varepsilon_e\varepsilon_h(V_D - V)}{q} \times \frac{(N_e+N_h)^2}{N_eN_h(N_h\varepsilon_h + N_e\varepsilon_e)}} \qquad (S22)$$

Table S1 Dielectric, ferroelectric and energy storage properties of some Aurivillius bismuth layer structured ferroelectric films.

Materials (films)	ε_r	E_{max} (kV/cm)	P_{max} (μC/cm^2)	P_{max}/E_{max} (μC/kV/cm)	U_{re}/E_{max} (J/cm^2/kV)	Ref.
$Bi_{3.25}La_{0.75}Ti_3O_{12}$	290	2040	60	0.029	0.022	1
$BaBi_4Ti_4O_{15}$	325	2000	50	0.025	0.022	2
$Ba_2Bi_4Ti_5O_{18}$	225	2340	39	0.0167	0.016	3
$Sr_2Bi_4Ti_5O_{18}$	165	2150	23	0.01069	0.008	3
$BaTiO_3$-$Bi_{3.25}La_{0.75}Ti_3O_{12}$	180	2800	42	0.015	0.019	4
$Na_{0.5}Bi_{3.25}La_{1.25}Ti_4O_{15}$	330	3300	72	0.022	0.022	This work
$BaBi_{3.4}Pr_{0.6}Ti_4O_{15}$	423	2049	87	0.0425	0.0419	This work

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