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Effects of Asymmetric Distribution of Charged Defects on the Hysteresis Curves of Ferroelectric Capacitors

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Abstract: When a ferroelectric film has an inhomogeneous distribution of charged defects, a voltage shift in the polarization curve is induced by the internal field generated in the film. The direction and the magnitude of voltage shift in the *P-V* hysteresis curves obtained by the Sawyer-Tower method are different from those obtained by the virtual ground method. In this study, the asymmetric behavior in the *P-V* hysteresis curves of inhomogeneous ferroelectric films was investigated with a physical model and the polarization curves obtained by the Sawyer-Tower and the virtual ground methods are compared.

Keywords: ferroelectric, modeling, Sawyer-Tower, virtual ground, hysteresis curve

1. Introduction

The polarization-applied voltage (*P-V*) hysteresis curves of ferroelectric capacitors are obtained either by Sawyer-Tower method or by virtual ground method. Inhomogeneous distribution of charged defects in ferroelectric film can alter apparent polarization values and induce a voltage shift in the polarization curve by the internal field generated in the film. The measurement of the direction and magnitude of the voltage shift is important in the study on the mechanism responsible for the asymmetric behavior in the ferroelectric capacitor. For example, when one wants to find out the mechanism of the hydrogen-induced degradation in the ferroelectric capacitor, he measures the direction and magnitude of the voltage shift in the *P-V* curves and the variation of polarization values with annealing time in a hydrogen-ambient.[1-3] In those studies, one must notice that the polarization values in hysteresis curve can be varied depending on the measurement method. Thus, it is meaningful to investigate how polarization values in the hysteresis curve of inhomogeneous ferroelectric film would vary when different measurement methods are applied. A physical modeling is useful for the study of the asymmetric behavior of ferroelectric capacitors. In this study, we obtained *P-V* curves for the inhomogeneous ferroelectric capacitors by calculating the local electric field and local polarization in asymmetric ferroelectric film with a physical model and studied the dependence of the measurement method on the voltage shift and polarization properties.

2. Modeling of *P-v* Curve

2.1 Modeling Procedure

A ferroelectric film is often considered to be a semiconductor with band gap of a few eV and its conductivity type is determined by the type of charged defects such as lattice vacancy or impurity. Studies on the ferroelectric capacitor have revealed that there is a Schottky contact between the ferroelectric film and the electrodes such as Pt and Ir and depletion layers are formed within the ferroelectric films.[4] Some researchers have reported that ferroelectric films with high dielectric constants are fully depleted when the density of charged defects and the

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film thickness are within a certain range. In this study, the density of charged defects and film thickness were selected to satisfy the full depletion condition according to Chai *et al.*[5)]

The ferroelectric capacitor diagram used in our model is shown in Fig. 1. The ferroelectric film with a thickness of d_f is divided into n sections to describe the ferroelectric film with inhomogeneous properties. When E_0, E_1, E_2, ⋯, and E_n are the local electric field at position x_0, x_1, x_2, ⋯, and x_n, respectively, Poisson's equation can be expressed as

$$\int_{E(x_0)=E_0}^{E(x_1)=E_1} dD = D(E_1)-D(E_0) = q\int_{x_0}^{x_1} N(x)dx \quad (1)$$

where D is electrical displacement, q is the electronic charge, and $N(x)$ is the density of charged defects. D is the sum of $\varepsilon_0 E$ and polarization P, and P is obtained by summing dipole switching polarization P_d and linear polarization $\varepsilon_0(\varepsilon_f - 1)E$, where ε_0 is the permittivity of free space, ε_f is the linear dielectric constant of the ferroelectric film, and E is electric field. P_d can be represented as a function of electric field with a modification of the functions as suggested by Miller *et al*[6)] as follows:

$$P_d^+(x) = P_s^+(x)tanh[(E(x)-E_c(x))/2\delta(x)] + (P_s(x)-P_s^+(x))$$

for a right-hand hysteresis curve (2a)

$$P_d^-(x) = P_s^-(x)tanh[(E(x)+E_c(x))/2\delta(x)] - (P_s(x)-P_s^-(x))$$

for a left-hand hysteresis curve, (2b)

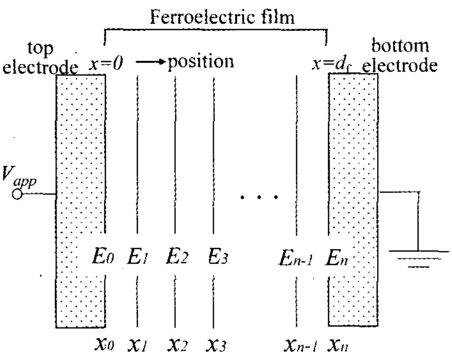

Fig. 1. The capacitor diagram used in our model. The ferroelectric film has a thickness of d_f. The interface with the top electrode is at $x = 0$ and the interface with the bottom electrode is at $x = d_f$. Voltage is applied to the top electrode and the bottom electrode is connected to ground.

where a right-hand hysteresis curve indicates the curve plotted when the applied voltage (V_{app}) is swept from $-V_{max}$ to $+V_{max}$, and the left-hand curve indicates the converse situation. The superscript + and – stand for a right-hand curve and a left-hand curve, respectively. $P_s(x)$ and $E_c(x)$ are the local saturation polarization and the local coercive field at x, respectively. $P_s^+(x)$ and $P_s^-(x)$ are the functions of the maximum electric field $E_{max}(x)$ as follows:

$$P_s^+(x) = \frac{P_s^-(x)tanh[(E_{max}^-(x)+E_c(x))/2\delta(x)] + P_s^-(x) - 2P_s(x)}{tanh[(E_{max}^-(x)+E_c(x))/2\delta(x)] - 1}$$

for a right-hand hysteresis curve (3a)

$$P_s^-(x) = \frac{P_s^+(x)tanh[(E_{max}^+(x)-E_c(x))/2\delta(x)] - P_s^+(x) + 2P_s(x)}{tanh[(E_{max}^+(x)+E_c(x))/2\delta(x)] + 1}$$

for a left-hand hysteresis curve (3b)

The function $\delta(x)$ is given as

$$\delta(x) = E_c(x)\{\ln[P_s(x)+P_r(x)/(P_s(x)-P_r(x))\}^{-1} \quad (4)$$

where $P_r(x)$ is the local remnant polarization at x. With a certain value of E_0 and given $N(x)$, $P_s(x)$, $P_r(x)$, $E_c(x)$, and $\varepsilon_f(x)$ functions, $P_s^+(x)$ and $P_s^-(x)$ can be calculated considering the electrical fields at $-V_{max}$ and $+V_{max}$, and then E_1 can be determined by solving eq. (1) numerically. E_2 can also be determined by setting the integration range from x_1 to x_2 in eq. (1). In this way, E_3, E_4, E_5, ⋯, and E_n can be determined and then the local potential $\phi(x)$ can also be determined. The appropriate E_0 can be determined by using the potential boundary conditions; $\phi(d_f) = 0$ and $\phi(0) = V_{app} + \Delta V_w$, where ΔV_w is the work function difference between the top and the bottom electrodes. Fig. 2 shows the process explained above. With this modeling method, $E(x)$, $P(x)$, $\phi(x)$ and *P-V* hysteresis curves can be determined for the ferroelectric film with any distributions of charged defects and inhomogeneous polarization parameters as a function of applied voltage. Further detailed explanation is presented elsewhere.[7)]

2.2 Plotting of *P-V* curve by the Sawyer-Tower method

The Sawyer-Tower circuit for plotting the *P-V* hysteresis curve of the ferroelectric film is shown in Fig. 3. The ferroelectric capacitor is connected to a paraelectric sense capacitor with a capacitance of C_{sense} in series and the voltage across the sense capacitor (V_{sense}) is measured as the driving voltage (V_{app}) is applied to these capacitors. Since the polarization of the ferroelectric film is $V_{sense} \cdot C_{sense}$, the *P-V* curve can be obtained by plotting $V_{sense} \cdot C_{sense}$ as a function of V_{app}. The driving voltage V_{app} is the sum of the voltage across the sense capacitor (V_{sense}) and the voltage across the ferroelectric film (V_f).

$$V_{app} = V_{sense} + V_f \quad (5)$$

V_f can be calculated by dividing the difference between the charge induced at the electrode (Q) and the charge induced by dipole switching polarization in the film(Q_p) by the linear capacitance of the ferroelectric capacitor (C_f). Q_p is $P_d \cdot A_f$ where A_f is the ferroelectric capacitor area and C_f is $e_0 e_f(A_f/d_f)$. Therefore, V_f can be expressed as follows:

$$V_f = \frac{Q - Q_P}{C_f} = \frac{Q - P_d A_f}{\varepsilon_0 \varepsilon_f (A_f/d_f)} \quad (6)$$

where d_f is the thickness of the ferroelectric film. Since the amounts of the charges induced at the electrodes are the same for both capacitors, Q can be represented as $V_{sense} \cdot C_{sense}$. When the capacitance ratio between the sense capacitor and the ferroelec-

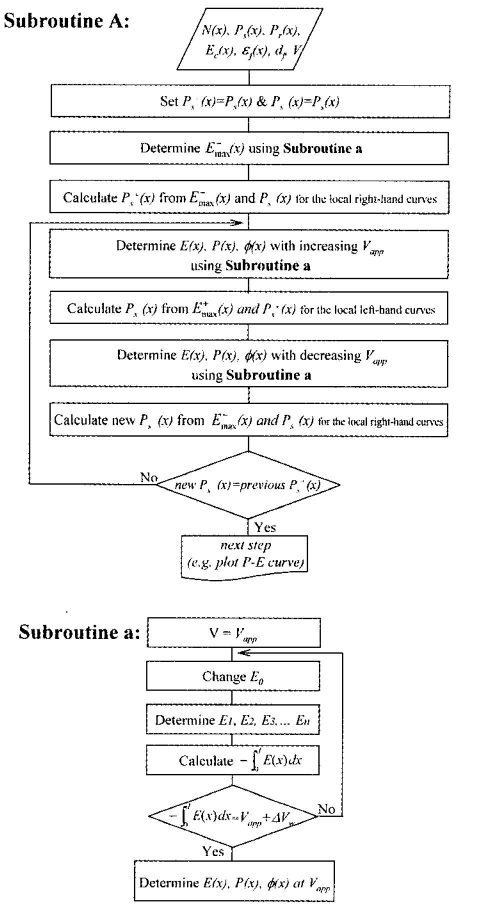

Fig. 2. The simulation process generating the *P-V* hysteresis curves.

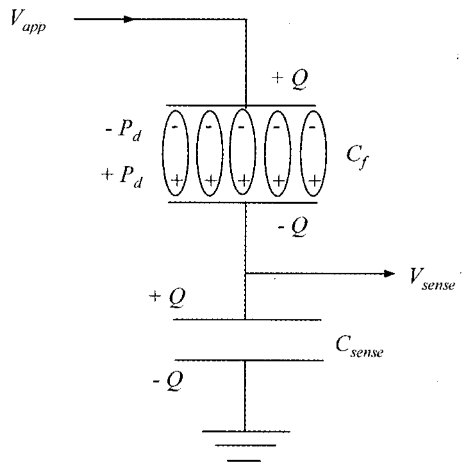

Fig. 3. Circuit diagram for the hysteresis curve measurement by the Sawyer-Tower method.

tric capacitor is denoted by a (i.e. $\alpha = C_{sense}/C_f$), eq. (5) yields

$$V_{app} = (\alpha + 1)V_{sense} - \frac{d_f}{\varepsilon_o \varepsilon_f}P_d \qquad (7)$$

The unknown variables in eq. (7) are V_{sense} and P_d. With a certain value of V_{sense}, the local electric field and local polarization in the ferroelectric film can be determined by using the simulation method described in the previous section under the following potential boundary conditions.

$$\phi(0) = V_{app} + \Delta V_w \qquad (8\text{-}1)$$
$$\phi(d_f) = V_{sense} \qquad (8\text{-}2)$$

P_d can be determined from the difference between the local polarization calculated considering P_d and the local polarization calculated without considering P_d. Thus, the value of V_{sense} that satisfies eq. (7) can be determined by iteration. Fig. 4 is a flow chart describing this process.

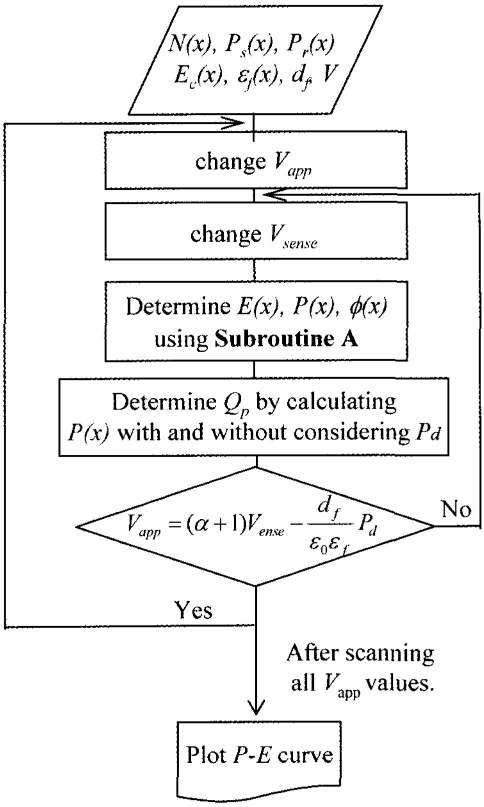

Fig. 4. The simulation process generating the P-V hysteresis curves for the Sawyer-Tower method.

2.3 Plotting of *P-V* curve by the virtual ground method

The circuit for plotting the P-V hysteresis curve by a virtual ground method is shown in Fig. 5. V_{app} applied to the ferroelectric film induces polarization in the film and moves charges to screen the polarization. The bottom electrode of the ferroelectric capacitor is connected to the input of the current amplifier. Since the voltage difference between the two terminals of an OP amp is zero, the bottom electrode of the ferroelectric capacitor is kept as the ground state. Therefore, the polarization value induced by V_{app} can be measured by integrating current generated in the circuit. In the virtual ground method, the curve starts from the origin since there is no variation in the charge distribution at the initial voltage condition, which is inconsistent with real polarization behavior. Thus, the measured curve is shifted to satisfy the condition of $|+P_{max}|=|-P_{max}|$, where $\pm P_{max}$ are the polarization values at $\pm V_{max}$.

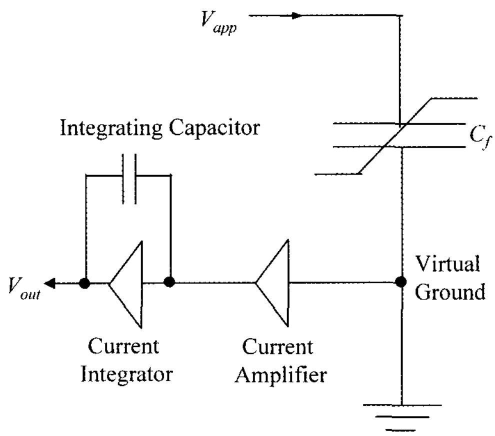

Fig. 5. Circuit diagram for hysteresis curve measurement by virtual ground method.

In the virtual ground method, one can avoid the error that is made by the sense capacitor in the Sawyer-Tower method. For most ferroelectric capacitors, the charged defect density and local polarization parameters are not homogeneous. Under these conditions, there is a difference between $|+P_{max}|$ and $|-P_{max}|$ which induces an error in measuring the voltage shift of the *P-V* curve. However, such effects can not be analyzed in the virtual ground method. In this study, the local polarization at the top surface of the ferroelectric film is calculated and then the variation is plotted with the applied voltage considering the condition of $|+P_{max}|=|-P_{max}|$ for the virtual ground method.

3. Results and Discussion

Asymmetric behaviors of *P-V* hysteresis curves for inhomogeneous ferroelectric capacitors were studied in Sawyer-Tower and virtual ground methods. The model parameters of the reference homogenous ferroelectric film were as follows: $N(x)$ of 1×10^{17} cm^{-3}, $P_s(x)$ of 45 $\mu C/cm^2$, $P_r(x)$ of 20 $\mu C/cm^2$, $E_c(x)$ of 60 kV/cm, and $\varepsilon_f(x)$ of 170. The inhomogeneous ferroelectric film was assumed to be composed of two regions whose model parameters are described as Boltzmann functions. Region 1, located near the top electrode, has the same model parameters as those of the reference film. Region 2, which has different model parameters from those used in the reference film, is located near the bottom electrode. When a ferroelectric film is deposited on the bottom electrode, the polarization properties of the initially deposited region are usually inferior to those of the overlying region, which is attributed to the nonstoichiometric composition and non-perovskite phase.[8,9] The model parameters of region 2 are as follows: $N(x)$ of 1×10^{19} cm^{-3}, $P_s(x)$ of 30 $\mu C/cm^2$, $P_r(x)$ of 10 $\mu C/cm^2$, $E_c(x)$ of 80 kV/cm, and $\varepsilon_f(x)$ of 100. The model parameters of region 2 are used independently or in combination as follows: case 1, when only $N(x)$ is different from that in the reference film; case 2, when polarization parameters except $N(x)$ are different from those in the reference film; case 3, when both $N(x)$ and polarization parameters are different from those in the reference film. In the Sawyer-Tower method, a was set as 1000 to remove the effect of the external depolarization field.

Fig. 6 shows the variation in the *P-V* curves of 200-nm-thick p-type ferroelectric capacitors having inhomogeneous model parameters with the measurement method when a maximum voltage of ±8 V is applied. The thickness of region 2 is 120 nm. The ferroelectric values (P_{max}, P_r, and ΔV_{shift}) are summarized in Fig. 7. ΔV_{shift} denotes the *P-V* curve shift

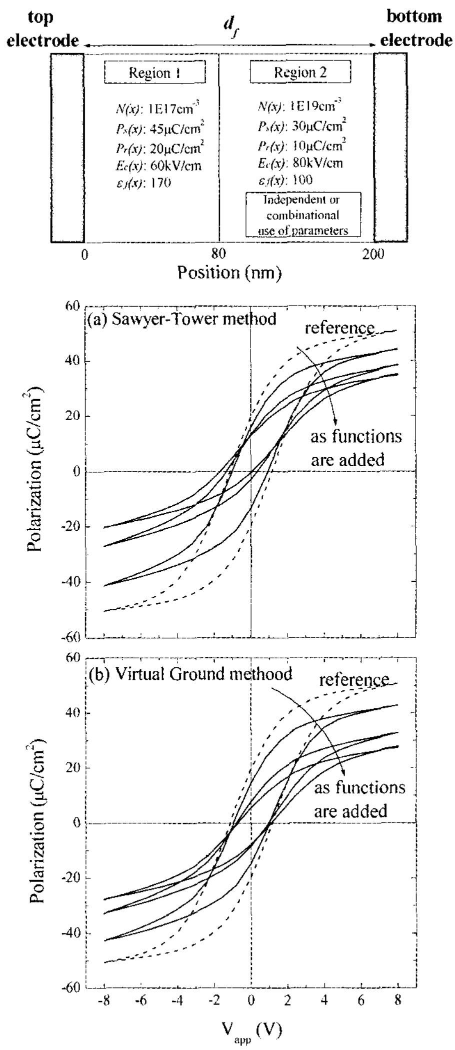

Fig. 6. Variation of the *P-V* hysteresis curve for the p-type ferroelectric film as the adopted model parameter functions are added: (a) the Sawyer-Tower method and (b) the virtual ground method.

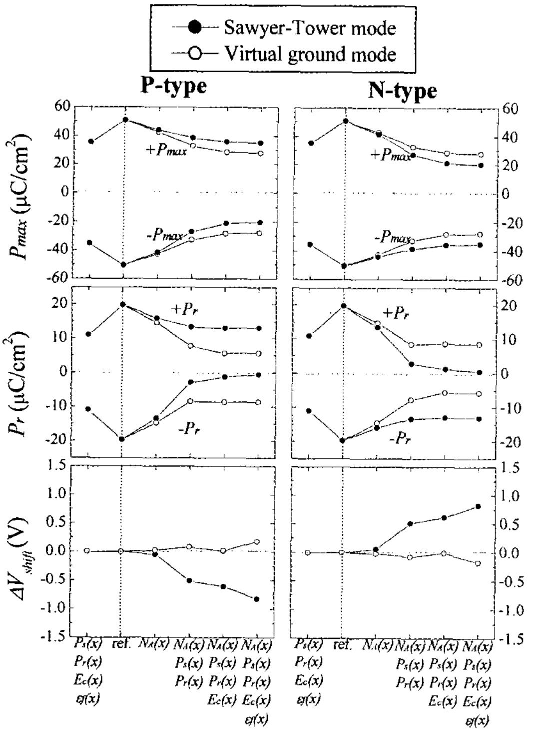

Fig. 7. Variations of apparent P_{max}, P_r and ΔV_{shift} as the adopted model parameter functions are added. Values of the apparent P_{max}, P_r and ΔV_{shift} are measured from the hysteresis curves in Fig. 6.

represented by $(|+V_c|-|-V_c|)/2$ where $+V_c$ and $-V_c$ are the positive ad negative coercive voltage, respectively. For the homogeneous reference sample, a symmetric *P-V* curve (i.e. $\Delta V_{shift} = 0$) is obtained and the curve shows no difference with the measurement method.

When the distribution of charged defect density ($N(x)$) is uniform and the local polarization functions ($P_s(x)$, $P_r(x)$, $E_c(x)$, and $e_f(x)$) are inhomogeneous, the hysteresis curves do not exhibit any voltage shift, while the apparent P_{max} and P_r values are decreased with respect to those of the reference curve. On the other hand, when the local polarization functions are homogeneous and the distribution of charged defect density is not uniform, the *P-V* curve shifted. This implies that the *P-V* curve shift primarily depends on the inhomogeneous distribution of $N(x)$. However, the magnitude of the voltage shift is only 0.05 V measured by the Sawyer-Tower method. When the inhomogeneity of the other local polarization parameters are combined, the voltage shift induced by the inhomogeneous charged defects is enhanced and the apparent polarization values are reduced. The *P-V* hysteresis curves obtained by the Sawyer-Tower method show that $|-P_{max}|$ decreases more rapidly than $|+P_{max}|$ for the p-type ferroelectric films (i.e. the type of the charged defect is an acceptor type), whereas $|+P_{max}|$ decreases more rapidly than $|-P_{max}|$ for the n-type ferroelectric films (i.e. the type of the charged defect is a donor type). This can be easily understood considering that the internal field induced by the inhomogeneous $N(x)$ is directed to the bottom electrode (i.e. positive internal field) for p-type film and to the top electrode (i.e. negative internal field) for n-type film. Therefore, the *P-V* curves register negative voltage shift (i.e. $|+V_c| < |-V_c|$) for p-type film and positive voltage shift (i.e. $|+V_c| > |-V_c|$) for n-type film. One needs to take notice that the magnitudes of the voltage shift obtained by the virtual ground method underestimated compared to those obtained by the Sawyer-Tower method. Furthermore, the direction of the voltage shift obtained by the virtual ground method is sometimes even opposite to that obtained by the Sawyer-Tower method.

The effect of the thickness ratio between region 1 and region 2 on the *P-V* curve was also studied. The thickness ratio was expressed as t/d_f, where t is the thickness of region 2. The model parameters of region 2 were set as follows: $N(x)$ of 1×10^{19} cm^{-3}, $P_s(x)$ of 30 $\mu C/cm^2$, $P_r(x)$ of 10 $\mu C/cm^2$, $E_c(x)$ of 80 kV/cm, and $\varepsilon_f(x)$ of 100. The variation of the polarization values and ΔV_{shift} in the *P-V* curves as a function of t/d_f are presented in Fig. 8. As t/d_f is increased, the apparent P_{max} value is decreased due to the reduced local electric field magnitude.[7] In the region where the magnitude of local electric filed is over 500 kV/cm, dipole switching polarization is saturated. Therefore, only a small value of linear polarization is induced by the additional applied voltage. Except for t/d_f values of 0 and 1, the hysteresis curves show voltage shift and the shift direction is

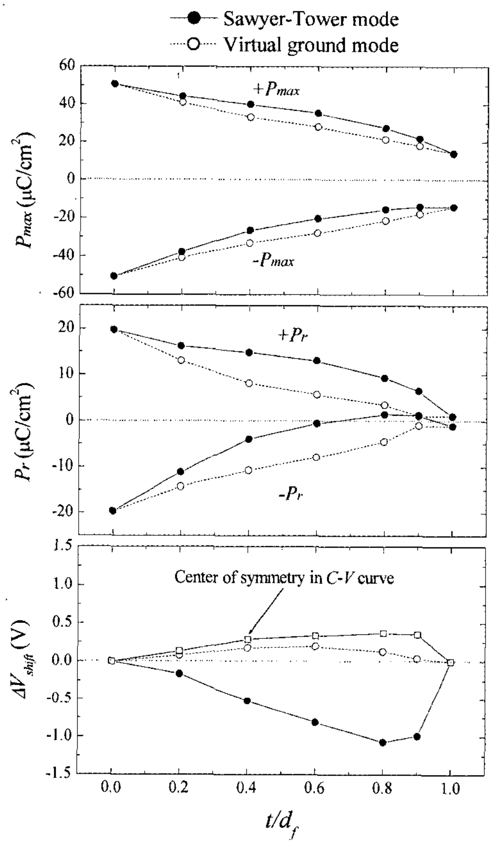

Fig. 8. Variations of apparent P_{max}, P_r and ΔV_{shift} with the thickness ratio t/d_f.

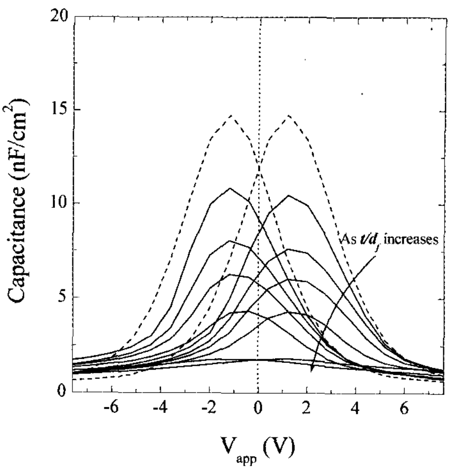

Fig. 9. C-V curves of the inhomogeneous ferroelectric film for various t/d_f values.

negative for the Sawyer-Tower method and positive for the virtual ground method. In addition, the maximum ΔV_{shift} is about -1 V for the Sawyer-Tower method, whereas it is below $+0.2$ V for the virtual ground method. Capacitance versus polarization (*C-V*) curve is plotted for various t/d_f values in Fig. 9. The center of symmetry (which is corresponding to the voltage shift in the *C-V* curve) is zero at $t/d_f = 0$ and 1. For other t/d_f values, the region with a relatively low increasing rate of polarization value is wide at the negative applied electric field, resulting in a positive center of symmetry. The voltage shift in the *C-V* curve is also shown in Fig. 8(c). The voltage shifts in the *C-V* curve and the *P-V* curve by the virtual ground method show the same tendency though their absolute values are slightly different.

The magnitude and direction of voltage shift in the *C-V* curve and in the *P-V* curve by the virtual ground method may be different from those in the *P-V* curve by the Sawyer-Tower method since the former is determined only by the shape asymmetry of the curves while the latter depends on the vertical shift and shape asymmetry of the curve. Therefore, the voltage shift in the *P-V* curve by the virtual ground method and the *C-V* curve cannot represent the real values.

4. Conclusion

A modeling method generating the *P-V* hysteresis curves by the Sawyer-Tower method and the virtual ground method was developed to investigate the degradation of remnant polarization by the asymmetric behavior of inhomogeneous ferroelectric film. When the ferroelectric film has an inhomogeneous distribution of charged defect in the film, the direction and the magnitude of voltage shift in the *P-V* hysteresis curves obtained by the Sawyer-Tower method are different from those by the virtual ground method. This is attributed to the fact that the voltage shift in the *P-V* curves by the Sawyer-Tower method are determined by both the vertical shift induced by the internal field and the shape asymmetry of the curve, whereas the voltage shift by the virtual ground method is only dependent on the shape asymmetry of the curve. For the same reason, the voltage shift obtained in the *C-V* curves shows the same tendency as in the *P-V* curves obtained by the virtual ground method.

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References

1. S. K. Hong, C. S. Hwang, O. S. Kwon and N. S. Kang, "Polarity-dependent rejuvenation of ferroelectric properties of integrated $SrBi_2Ta_2O_9$ capacitors by electrical stressing", Appl. Phys. Lett., 76, 324 (2000).
2. T. Tamura, K. Matsuura, H. Ashida, K. Kondo and S. Otani, "Hysteresis variations of (Pb, La)(Zr,Ti)O_3 capacitors baked in a hydrogen atmosphere", Appl. Phys. Lett., 74, 3395 (1999).
3. D. C Kim, K. S. Choi, K. W. Lee and W. J. Lee, "Effects of remanent polarization state and internal field in ferroelectric film on the hydrogen –induced degradation characteristics in Pt/Pb(Zr,Ti)O_3/Pt capacitors ", J. Kor. Inst. Met. & Mater., 12, 75 (2002).
4. K. Watanabe, A. J. Hartmann and R. N. Lamb, "Electronic characteristics of the $SrBi_2Ta_2O_9$–Pt junction", J. Appl. Phys., 84, 2170 (1998).
5. F. K. Chai, J. R. Brews, R. D. Schrimpf and D. P. Birnie, "Limitations of the uniform effective field approximation due to doping of ferroelectric thin-film capacitors", J. Appl. Phys., 78, 4766 (1995).
6. S. L. Miller, J. R. Schwank, R. D. Nasby and M. S. Rodgers, "Modeling ferroelectric capacitor switching with asymmetric nonperiodic input signals and arbitrary initial conditions", J. Appl. Phys., 70, 2849 (1991).
7. Y. I. Kim and W. J. Lee, "Modeling of hysteresis curves of ferroelectric capacitor with inhomogeneous charged defect density and polarization parameters in the ferroelectric film", Jpn. J. Appl. Phys., 39, 1309 (2000).
8. J. S. Shin and W. J. Lee, "A comparative study on the nucleation and growth of ECR-PECVD PLZT ((Pb,La)(Zr,Ti)O_3) thin films on Pt/SiO_2/Si substrates and on Pt/Ti/SiO_2/Si substrates", Thin Solid Films, 333, 142 (1998).
9. S. O. Chung, J. W. Kim, S. T. Kim, G. H. Kim and W. J. Lee, "Microstructure and electric properties of the PZT thin films fabricated by ECR PECVD: the effects of an interfacial layer and rapid thermal annealing", Mater. Chem. & Phys., 53, 60 (1998).