CHARACTERIZATION AND MODELLING OF THIN-FILM FERROELECTRIC CAPACITORS USING C-V ANALYSIS

CIARAN J. BRENNAN
The Charles Stark Draper Laboratory, Inc., 555 Technology Square, Cambridge, MA U.S.A

Abstract Advances have been made in the electronic characterization and analysis of thin-film ferroelectric (FE) memory capacitors using capacitance vs. voltage (C-V) measurements. A mathematical model of the small-signal electrical behavior of the FE capacitor has been developed. This analysis shows that the small-signal characteristics of the FE capacitor are largely determined by the space charge concentrations at the ferroelectric to contact interface. These space charge regions have an adverse effect on the permittivity, coercivity and switching characteristics of the ferroelectric capacitor. These results will contribute to improving ferroelectric processing, appraising the quality of ferroelectric devices, and developing device models of the ferroelectric memory capacitors for use in circuit design.

INTRODUCTION

This work is focused on developing a thorough interpretation of the C-V measurements and their implications. Previous work on C-V analysis has been largely qualitative in nature[1-3]. The theory of the semiconductor behavior of thin-film ferroelectrics has been used to develop a mathematical model to explain and analyze the C-V data.

Outline:
1) The interaction between the dielectric switching of the ideal ferroelectric and the space-charge regions at the contacts are presented.
2) An analytical model for the small signal C-V characteristics is developed. The C-V behavior and the switching of the polarization are shown to be modulated by the space charges.
3) The significance of the model to ferroelectric device characterization is discussed.

FERROELECTRIC SWITCHING AND SPACE CHARGES

Simple model of switching permittivity:
This analysis employs a simplified model for the switching dielectric properties of the ferroelectric. A more rigorous and complete model of the switching dielectric properties has been derived from the free energy expression and will be presented in an upcoming article.

The ferroelectric permittivity K is very large in a small region about the coercive field value ($E_C \pm \delta$) due to the switching of the domains. This occurs because during switching a very small change in the applied electric field results in a very large change in the ferroelectric polarization. Peak permittivity values of 5,000 or more can be obtained in high-quality samples.[6,7] In the limit that $K(E_C) \rightarrow \infty$ and $\delta \rightarrow 0$, the following expression using the Kronecker delta function describes the permittivity K. The negative sign in the delta function is used when the applied field is increasing in the positive direction; the positive sign is used in the negative direction. K_0 is a constant which approximates the non-switching permittivity.

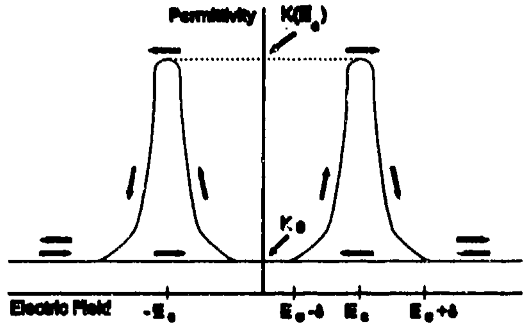

Figure 1 *Diagram of permittivity vs. electric field for the idealized ferroelectric.*

$$K = K_0 + \left[K(E_C) - K_0\right] \cdot \delta(E \pm E_C) \tag{1}$$

Space Charge Effects:

Ferroelectrics ceramics have a large bandgap (3 to 5 eV) and are normally considered insulators. However, the large value of spontaneous polarization of the ferroelectric tends to produce immense electric fields at the surface of the ferroelectric crystal. This electric field causes strong band bending and the ionization of trap states in the surface region of the ferroelectric regardless of the size of the bandgap. This ionization continues until a surface space charge develops of sufficient magnitude to screen the internal polarization of the ferroelectric.[8,9]

The metallic electrodes in a ferroelectric capacitor form Schottky contacts. The space charge accumulation at the interface is due to the band-bending caused by the Schottky potential, the spontaneous polarization, and the applied bias[9,10] (Figure 2). The depolarizing field in the ferroelectric is produced by the difference in space charge concentrations at the two junctions. Net charge neutrality is maintained by opposing electron concentrations in the metal contacts.

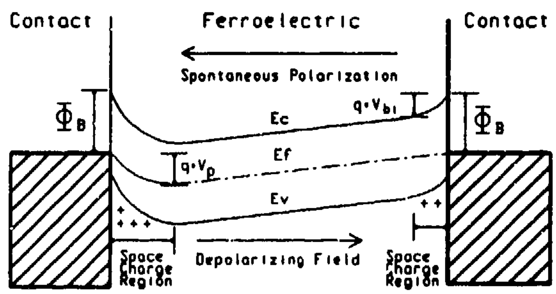

Figure 2 *Band-bending in the ferroelectric capacitor due to the Schottky barriers and the spontaneous polarization.*

Charge-Compensation Effects:

The electric field is not a linear function of distance in the ferroelectric because K is a function of the electric field. Therefore Poisson's equation must be rewritten:

$$\nabla \cdot E = \frac{\rho}{K(E)\varepsilon_0} \tag{2}$$

Integrating, we get:

$$E = \int \frac{\rho}{K(E)\,\varepsilon_0} \cdot dx \tag{3}$$

The electric field changes slowly in the regions where K is large, i.e., when E is in the neighborhood of the coercive field value. Figure 3 is a plot of the electric field as a function of the distance through the ferroelectric as given in Equation (3).

The *neutral region* is defined as the region in which the electric field is in the vicinity of its coercive value. The *space charge regions* are defined as the areas at each contact where the electric field is large enough to saturate the ferroelectric ($E > E_C+\delta$). Ionized traps may be present in the neutral region. However, the contribution of the ionized traps to the electric field are almost completely compensated by the large polar displacement of the ferroelectric.

The compensation of the ionized charge by the ferroelectric is important; only the neutral region of the ferroelectric has a large permittivity value - the space charge regions at the contacts have the much lower saturated permittivity. The ferroelectric capacitor is a three-layer dielectric sandwich, that is, a high-permittivity layer between two low-permittivity layers. This is the primary insight in the ferroelectric model which follows. By determining the widths of the space charge under bias one can accurately predict the electrical characteristics of the ferroelectric capacitor.

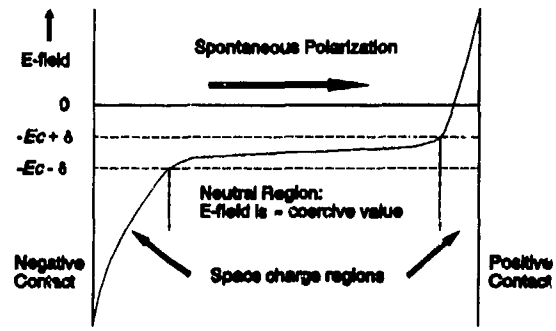

Figure 3 *Electric field as a function of distance in the ferroelectric.*

THE FERROELECTRIC C-V MODEL

Assumptions:

The assumptions for the ferroelectric model are drawn from the discussion above.

1) The ferroelectric has the properties of a wide-bandgap semiconductor. The occupancy of trap states near the band edges changes as a function of the Fermi energy.

2) A metal contact to the ferroelectric forms a Schottky contact with a characteristic Schottky barrier ϕ_B. The difference between the work function of the metal and the electron affinity of the ferroelectric make the metal the anode and the ferroelectric the cathode.

3) Any surface states at the metal-ferroelectric junction can be adequately characterized as a static shift in ϕ_B. No dynamic effects involving the change in occupancy of surface states are considered.

4) The permittivity of the ferroelectric is given by (1). The permittivity is characterized by high peak values around the coercive field E_C, hysteresis, and a lower saturated permittivity for $E >> E_C$.
5) The concentration of immobile ionized states ρ is constant.

Measurements:
All the data for the C-V measurements were taken from a commercial ferroelectric memory integrated circuit. The memory capacitors were measured by probing the integrated circuit. These ferroelectric devices employ a PZT ferroelectric with ruthenium oxide contacts. The capacitors measured 20 microns by 20 microns. All measurements were taken at room temperature.

The Model:
The small-signal C-V model simultaneously solves for the voltages across the space charge regions and the spontaneous polarization across the neutral region. We consider the applied voltage V_{ap}, the voltages across the two space charge regions V_{sc1} and V_{sc2}, and the voltage developed by the spontaneous polarization in the neutral region V_{pol}. The sum of the voltages across the two space charge regions and the voltage across the neutral region is equal to the total voltage applied.

The capacitance of the thin-film ferroelectric capacitor is modelled as the series capacitance of the two space charge and the neutral regions. Because the permittivity of the neutral region is very large compared to the space charge regions, the series capacitance of the neutral region can generally be ignored. The capacitance of the space charge regions follow the formula for Schottky contacts:

$$C_{sc} = \sqrt{\frac{q K \varepsilon_0 N}{2 (V_{sc})}} \tag{4}$$

C_{sc} is the capacitance per unit area across the space charge region, N is trap concentration which is assumed to be equal to the ionized charge density ρ, and V_{SC} is the potential across the space charge region at the junction.

The width of the space charge region W_{sc} is given by:

$$W_{sc} = \sqrt{\frac{2 V_{sc} K \varepsilon_0}{q N}} \tag{5}$$

The total capacitance C_{tot} for the ferroelectric capacitor is equal to the series capacitances of the two space charge region C_{sc1} and C_{sc2} and the capacitance of the neutral region C_{neut}:

$$C_{tot} = \frac{1}{\frac{1}{C_{sc1}} + \frac{1}{C_{sc2}} + \frac{1}{C_{neut}}} \tag{6}$$

To calculate the capacitance of the ferroelectric device as a function of voltage, the values of C_{sc1}, C_{sc2}, and C_{neut} must be determined. The capacitance values can be calculated from the voltages V_{sc1}, V_{sc2}, and V_{pol}. The sum of these voltages must equal the applied voltage V_{ap}:

$$V_{ap} = V_{sc2} - V_{sc1} + V_{pol} \tag{7}$$

V_{sc1} and V_{sc2} have opposite polarities because the two junctions face in opposite directions.

Equation (7) serves as one constraining equation for the problem. The second constraining equation is simply charge conservation. Therefore, the problem of calculating the C-V behavior of the ferroelectric capacitor boils down to determining how the applied voltage is split between the space charge regions and the spontaneous polarization.

Obtaining the solution is simplified by examining three different voltage ranges: (1) $V_{ap} < 0$, (2) $0 \le V_{ap} \le 2 \cdot VPOL$, (3) $V_{ap} > 2 \cdot VPOL$ ($VPOL$ is the maximum value of the spontaneous polarization V_{pol}). The divisions were selected assuming that the ferroelectric capacitor has been polarized in the negative direction and that the applied voltage is increasing from a negative value to a positive value. If the capacitor was polarized in the positive direction, the three voltage ranges would be chosen with the opposite polarity.

$\underline{V_{ap} \le 0}$:

Assume that the ferroelectric capacitor has been fully polarized to its negative state. The negatively biased contact (contact 1) is reverse biased by V_{ap}, V_{pol}, and the Schottky potential ϕ. The other contact (contact 2) is assumed to be at ground potential. Contact 2 is forward biased, and the voltage across it is the Schottky potential only, so its capacitance is constant. The C-V behavior in this voltage range is governed by the width of the space charge at contact 1, the only quantity affected by the applied voltage.

The voltages across the three regions of the ferroelectric are: $V_{pol} = VPOL$; $V_{sc2} = \phi$; $V_{sc1} = -V_{ap} + V_{pol} + \phi$. Using (4) and (6), the overall capacitance is given by:

$$C_{tot} = \frac{1}{\dfrac{1}{\sqrt{\dfrac{qK\varepsilon_0 N}{2(-V_{ap} + VPOL + \phi)}}} + \dfrac{1}{\sqrt{\dfrac{qK\varepsilon_0 N}{2\phi}}}} \tag{8}$$

The C-V curve of the ferroelectric capacitor follows the Schottky model closely in this region, and provides a good fit to the experimental data (given appropriate choices for $VPOL$, ϕ, and N).

Equation (8) may be used to extract values for ϕ and N from experimental data. ϕ and N are extracted by iteratively optimizing the fit between (8) and the experimental C-V data for the voltage range between the maximum applied voltage and zero.

$\underline{0 \le V_{ap} \le 2 \cdot VPOL}$:

The significant event which occurs over the voltage range $0 \le V_{ap} \le 2 \cdot VPOL$ is the transfer of the space charge between the contacts. As the applied voltage sweeps across this range, the space charge is transferred from the first contact to the second contact. No switching of the ferroelectric occurs because the neutral region is shielded from the applied voltage by the redistributed space charge.

First, we must look at the endpoints of this voltage range. When $V_{ap} = 0$, (7) gives:

$$\begin{aligned} V_{scl} &= \phi + VPOL \\ V_{sc2} &= \phi \end{aligned} \tag{9}$$

The spontaneous polarization *VPOL* maintains the equal and opposite space charge voltage V_{scl}. When V_{ap} increases in the positive direction, contact 2 becomes reverse biased, and the reverse bias on contact 1 is reduced. The space charge on contact 1 shrinks while the space charge at contact 2 grows by an equal amount, as required by charge conservation. When $V_{ap} = 2 \cdot VPOL$, (7) gives:

$$\begin{aligned} V_{scl} &= \phi \\ V_{sc2} &= V_{ap} + V_{scl} - V_{pol} = VPOL + \phi \end{aligned} \tag{10}$$

V_{scl} is now equal to its equilibrium voltage ϕ, and V_{pol} is still equal to its maximum value *VPOL*. Contact 1 is no longer reverse biased, and all the space charge that was at contact 1 has been transferred to contact 2. The applied voltage $2 \cdot VPOL$ is opposed both by the polarization voltage V_{pol} and an additional space charge voltage equal to *VPOL* at contact 2.

The numerical solution to this problem requires two constraints. The first is (7), which establishes the sum of the voltages. The second constraint is charge conservation; the space charge removed from contact 1 must be gained by contact 2. If the space charge regions are assumed to have a constant charge density, the total width of the space charge regions is constant over this range:

$$W_{scl}(V_{ap}) + W_{sc2}(V_{ap}) = W_{scl}(0) + W_{sc2}(0) \tag{11}$$

Using (5) and (11) we get an expression for the voltage across one space charge in terms of the voltage across the other:

$$V_{scl}(V_{sc2}) = \frac{N}{C_X} \cdot \left[W_{scl}(0) + W_{sc2}(0) - \sqrt{\frac{C_X}{N} \cdot V_{sc2}} \right]^2 \tag{12}$$

C_X is just the collection of constants in (5):

$$C_X = \frac{2 \cdot K \cdot \varepsilon_0}{q} \tag{13}$$

$W_{scl}(0)$ and $W_{sc2}(0)$ are found by inserting the conditions for $V_{ap}=0$ given in (9) into the equation for space charge width (5). Equations (7) and (12) are combined to find V_{scl} and V_{sc2}. This is done by numerically solving for the root of the following equation:

$$V_{sc2} = \mathrm{ROOT}\,(V_{ap} - VPOL - V_{sc2} + V_{sc1}(V_{sc2})) \tag{14}$$

The ROOT function varies V_{sc2} until the expression in parentheses equals zero. The value found for V_{sc2} is then inserted into (12) to find V_{sc1}. After the space charge voltages have been found, the Schottky capacitance equations (4) and (6) are applied to find the small-signal capacitance.

<u>$V_{ap} > 2 \cdot VPOL$:</u>

When the applied voltage exceeds $2 \cdot VPOL$, the space charge at contact 2 increases with the applied voltage, and the space charge at contact 1 remains at the minimum width established by the Schottky potential ϕ. The polarity of the ferroelectric region engulfed by space charge 2 is switched by the large electric field in the space charge. The ferroelectric in the neutral region retains its original polarity. The voltage due to spontaneous polarization V_{pol} diminishes and then reverses sign as the neutral region is engulfed by space charge 2. When the applied voltage reaches the point where the space charge extends all the way across the ferroelectric, the switching of the ferroelectric is complete.

For this voltage range, V_{sc1} is constant and equal to ϕ, so the width of space charge 1 (W_{sc1}) is constant. The width of space charge 2 (W_{sc2}) is determined by the voltage drop across that space charge.

$$\begin{aligned} W_{sc1} &= \sqrt{\frac{C_X}{N} \cdot \phi} \\ W_{sc2} &= \sqrt{\frac{C_X}{N} \cdot V_{sc2}} \end{aligned} \tag{15}$$

V_{pol} and V_{sc2} are the two unknowns. Since V_{pol} is determined by the W_{sc2}, which in turn is determined by V_{sc2}, we can write V_{pol} as a function of V_{sc2}:

$$V_{pol} = VPOL \cdot \left[\frac{W_{tot} - 2 \cdot W_{sc2}(V_{sc2})}{W_{tot} - 2 \cdot W_{sc1}} \right] \tag{16}$$

This equation calculates V_{pol} in terms of the fraction of the neutral zone which is engulfed by space charge 2. Equations (16) and (7) are combined and the root is found numerically:

$$\begin{aligned} V_{sc2} &= \mathrm{ROOT}[V_{ap} - V_{pol}(V_{sc2}) - V_{sc2} + V_{sc1}] \\ V_{sc1} &= \phi \end{aligned} \tag{17}$$

Once the space charge voltages have been found, the overall capacitance is calculated using the equations for the Schottky junction capacitance (4) and (6).

RESULTS

The results of the C-V model for one sweep vs. the experimental data is shown in Figure 4. The fit of the calculated curve is excellent for applied voltages less than -*VPOL*. This indicates that the Schottky contact model for the capacitance is a good one for this voltage range. The following device parameters were extracted from the C-V data: ϕ = .55v, $VPOL$ = .65v, $N = 4{\cdot}10^{18}/\text{cm}^3$, K_0=400.

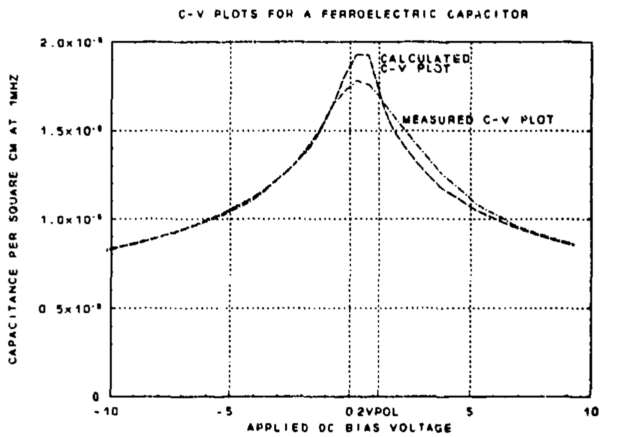

Figure 4 *The calculated C-V plot without compensation for finite permittivity.*

However, the calculated curve deviates from the experimental data for positive applied voltages. Two effects can be observed here. First, the peak calculated capacitance, which occurs in the range $-VPOL \leq V_{ap} \leq 2{\cdot}VPOL$, is significantly greater than the measured peak capacitance. Second, the calculated capacitance is lower than the measured capacitance for much of the range $V_{ap} > 2{\cdot}VPOL$.

The anomalous calculated peak capacitance is due to the fact that the series capacitance of the neutral region has been ignored in the previous calculations. When the applied bias is less than the coercive voltage, the permittivity of the ferroelectric in the neutral region declines, and the series capacitance of the neutral region cannot be ignored. The permittivity of the ferroelectric under these bias conditions can be inferred from the difference between the theoretical and measured C-V plots. The adjusted value of the permittivity (K_{eff}) for the low field condition can be calculated by adding the effective capacitance of the neutral region in series with the small signal capacitance of the two space charge regions (C_{tot}).

$$\frac{1}{\dfrac{1}{C_{tot}} + \dfrac{1}{\left[\dfrac{K_{eff}\cdot\varepsilon_0}{W_{tot} - W_{sc1} - W_{sc2}}\right]}} = C_{measured} \tag{18}$$

This calculation yields $K_{eff} \approx 5000$ for $0 < V_{ap} < VPOL$, and $K_{eff} \approx 10{,}000$ for $-VPOL < V_{ap} < 0$ or $VPOL < V_{ap} < 2{\cdot}VPOL$. This shows that the permittivity of the neutral region, though always very large, is at its minimum under low biases that are not strong enough to maintain the coercive field (Figure 5).

The second discrepancy between the calculated and measured C-V curves occurs at voltages above $2{\cdot}VPOL$, where the measured capacitance values are significantly greater than the calculated values. The capacitance readings of the samples tested were observed to decrease steadily over a period of several minutes when held at a constant DC bias. The C-V plots shown here, on the other hand, were taken with a constant bias voltage sweep rate of 50 mV per second. These preliminary observations indicate that the measured C-V plot falls much closer to the calculated curve if the capacitance measurement is allowed to stabilize for several minutes at each value of the bias voltage. The slow relaxation of the dielectric properties of the ferroelectric has been attributed to the slow thermalization of deep electron states in the ferroelectric[11-13].

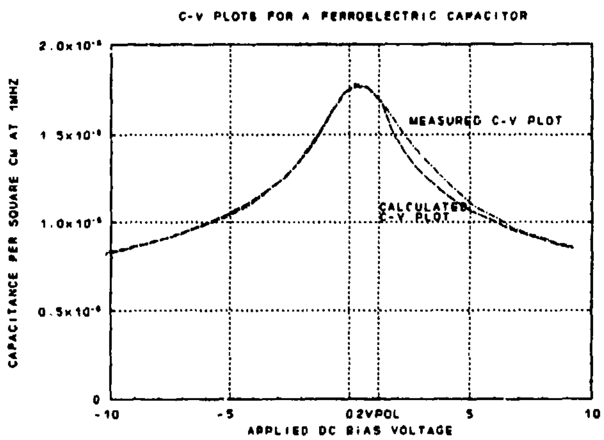

Figure 5 *C-V plot compensated for finite permittivity at low bias voltages.*

CONCLUSION

A model has been derived for the small-signal capacitance vs. voltage (C-V) characteristics of the thin-film ferroelectric capacitor. The ferroelectric capacitor is analyzed from first principles in terms of the interactions between the polar dielectric properties of the ferroelectric and the space charge regions which form due to its semiconducting properties. The ferroelectric capacitor is shown to obey the ideal Schottky contact C-V behavior over the non-switching portion of the cycle. During the switching portion of the voltage sweep, the partial switching of the ferroelectric is shown to be governed by the expansion of the space charge regions. The size of the space charge regions, in turn, is affected by the polarization of the ferroelectric.

This model has a number of immediate applications. First, the C-V model can be used to extract important device parameters: the trap concentration, which indicates the quality of the ferroelectric; the Schottky barrier potential, which permits an appraisal of the metallization quality; the maximum spontaneous polarization; and the saturated permittivity of the ferroelectric. Second, the model gives an accurate way to infer the characteristics of the space charge regions, which are thought to play a significant role in the aging and wear-out of ferroelectric devices[14-16]. Monitoring the C-V characteristics during aging and endurance cycling will provide a means to test those hypotheses. Third, this small-signal model will constitute a significant part of a more complete model in the future, which will be used for circuit-level design work.

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