Mitigating the dead-layer effect in nanocapacitors using graded dielectric films

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As ideal candidates for next-generation energy storage devices, nanocapacitors are predicted to exhibit very high capacitance according to classical theory. However, the actual capacitance of nanocapacitors is dramatically lower than expected. This is attributed to the so-called ‘dead-layer’ effect associated with the flexoelectricity of dielectric films and the incomplete screening of metal electrodes. In this paper, a way to mitigate this negative effect is demonstrated by using graded dielectric films instead of homogeneous films. The enhancements due to grading dielectric films were obtained by using perturbation theory to solve the governing equations with boundary conditions in Mindlin’s model of parallel-plate capacitors. We have shown that by grading both the relative permittivity and the elastic constant, we can obtain enhancement of almost 27% in capacitance for the 2.7 nm SrTiO3 dielectric film. In addition, the impact of various dielectric film properties on the overall capacitance was investigated.

Keywords: nanocapacitor; dead-layer effect; graded dielectric film

1. Introduction

Nanocapacitors have received considerable attention in recent years due to the promises of high energy and power densities and utilization in nanoelectronic applications [1–3]. Using high dielectric constant materials (i.e. BaTiO3 and SrTiO3 with perovskite structures [4]) and nanoscale dielectric films, the capacitance of nanocapacitors can theoretically approach very high levels. However, there are certain challenges and bottlenecks that must be overcome [5,6]. Several studies have addressed design, materials and fabrication issues associated with nanocapacitors [7–10], unexpected low capacitance or ‘dead-layer’ effect [11,12], and quantum electrical phenomena in nanocapacitors [13,14]. In this study, we focused on mitigating the ‘dead-layer’ effect by grading the dielectric film properties.

The promise of high energy density in nanocapacitors emerges from basic capacitance and energy storage theories. Since the classical capacitance is inversely proportional to the distance between the parallel plates and the energy stored in a capacitor is directly proportional to the capacitance, the microscale to nanoscale transition in capacitors should lead to several orders of magnitude increase in capacitance and significant enhancement in energy storage. However, experimental measurements have shown rather unexpected results and the capacitance of nanocapacitors is found to be much lower than that predicted by classical theories [15–17]. A recent ab initio simulation by Stengel and Spaldin [18] has...
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verified that for a 2.7 nm SrTiO\textsubscript{3} (STO) capacitor, the actual capacitance is 258 fF \(\mu\text{m}^{-2}\) rather than the classical theory prediction which is 1600 fF \(\mu\text{m}^{-2}\) (Figure 1a). It appears as if a layer of very low permittivity (‘dead layer’) with capacitance \(C_i\) is present at the metal/dielectric interface and when in series with the dielectric film \((C_d)\), it can cause a dramatic drop in the overall capacitance, \(C_{\text{eff}}\):

\[
\frac{1}{C_{\text{eff}}} = \frac{1}{C_i} + \frac{1}{C_d} + \frac{1}{C_i}.
\]

and hence the term ‘dead layer’ has been coined in relation to this observed phenomenon [19–21]. The cause of dead-layer effect was initially attributed to material defects, but an improved manufacturing process [22] disproved this notion, verified by the \textit{ab initio} simulation [18], and the problem of low capacitance continued to persist even in defect-free nanocapacitors.

Recent studies have identified two main causes for the ‘dead-layer’ effect: flexoelectricity and incomplete screening. Flexoelectricity refers to the behavior of centrosymmetric, non-piezoelectric materials (Figure 1b) that if subjected to non-uniform strain can exhibit polarization [23,24]. Incomplete screening refers to the phenomenon where the electric field penetrates into the metal, as shown in Figure 1c [11].

In order to mitigate the ‘dead-layer’ effect in nanocapacitors, we can focus on either the electrodes or the dielectric films. The results of the \textit{ab initio} simulation by Stengel and Spaldin [18] indicated that using metals such as Pt or Au with shorter electronic screening length could reduce the dead-layer effect. On the other hand, since graded materials have been used to improve mechanical and electrical performances [25], in this study, we explore graded dielectric films to enhance the capacitance of nanocapacitors.

Figure 1. (a) Classical capacitance (per unit area) prediction \((C = \varepsilon/d, \varepsilon_r = 490)\), at nanoscale dielectric film lengths and \textit{ab initio} simulation result. (b) Schematics of centrosymmetric non-piezoelectric material exhibiting polarization when subjected to non-uniform strain. (c) Incomplete screening caused by electric field penetration into electrode metal.
2. Theoretical analysis

Capacitance is defined as the ratio of free charge to the voltage drop. Using Gauss’s law, we can relate the electric field, $E$, polarization vector, $P$, and permittivity, $\varepsilon_0$, to free charge density, $\rho_f$, in the capacitor:

$$\nabla \cdot (\varepsilon_0 \vec{E} + \vec{P}) = \rho_f.$$  
(2)

The term inside the parenthesis in Equation (2) is known as the electric displacement, $\vec{D}$.

For a parallel-plate capacitor, the magnitude of electric displacement is equal to the free charge density at the plate surface and the direction is from positive to negative electrode. Therefore, the specific capacitance can be expressed as:

$$C_s = \frac{D}{V}.$$  
(3)

2.1. Homogeneous dielectric film

For the homogeneous dielectric film capacitor system illustrated in Figure 2, we can use Mindlin’s model [26,27] for the one-dimensional (1D) case to describe the relations between three independent fields, namely displacement $u$, polarization $P$, and electric potential $\phi$. The governing equations (GE) can be expressed as:

$$\begin{align*}
    c \partial^2 u + d \partial^2 P &= 0 \\
    d \partial^2 u + b \partial^2 P - \alpha P - \partial \phi &= 0, \\
    -\varepsilon_0 \partial^2 \phi + \partial P &= 0
\end{align*}$$  
(4)

where $c$ is the elastic constant, $d$ is a coupling factor that addresses both polarization-gradient to strain and polarization to strain-gradient coupling, $b$ is the polarization-gradient coupling factor, and $\alpha$ is the reciprocal dielectric susceptibility ($\varepsilon_0 \alpha = \eta^{-1}$) [26].

The boundary conditions (BC) are

$$\begin{align*}
    (c \partial u + d \partial P)_{x=\pm h} &= 0 \\
    P(-h) &= P(h) = -\frac{\varepsilon_0 k h V_d}{h} \\
    (\phi)_{x=\pm h} &= \pm V_d
\end{align*}$$  
(5)

where $h$ is the half thickness of the dielectric film, $k$ is the penetration constant, $\eta$ is the dielectric susceptibility, and $V_d$ is the voltage at the metal electrodes. The parameter $k$ controls the depth at which the electric field penetration occurs [27,28].

Figure 2. Schematic of a parallel-plate capacitor.
The solution to the specific capacitance is obtained as:

\[
C_{s0} = \frac{\varepsilon_0 \partial \phi - P}{2V_d} = \frac{\varepsilon_0 \varepsilon_r}{2h} \left( 1 + \frac{h}{h'} \right) \tanh \left( \frac{h}{h'} \right) = \frac{\varepsilon_0 \varepsilon_r}{2h} \left( \frac{h}{h'} \right) + \left( \frac{h}{h'} \right) \tanh \left( \frac{h}{h'} \right),
\]

where \( \varepsilon_r \) is the relative permittivity and

\[
l = \sqrt{\frac{(b - d^2/c)}{(a + 1/\varepsilon_0)}}.
\]

The parameter \( l \) is defined as the longitudinal flexoelectric length scale and it is a real number due to the positive definiteness of energy density [26]. This solution can be found in Mindlin’s papers [26,27] and recent work by P. Sharma’s group [28].

2.2. Graded dielectric film

In order to increase the effective capacitance, the properties of the dielectric film are graded (Figure 3a) with a linear grading function, as depicted in Equation (8) and Figure 3b:

\[
g(x) = w \left( \frac{x + h}{h} \right).
\]
where $w$ is the grading direction. The main graded properties are relative permittivity $\varepsilon_r$ and elastic constant $c$:

$$\varepsilon_r = \varepsilon_{r0} \{1 + \lambda g(x)\}; \, 0 \leq \lambda \leq 1,$$

(9)

$$c = c_0 \{1 + \lambda g(x)\},$$

(10)

where the subscript 0 represents the original (ungraded) parameters. The overall capacitance of a graded film can be determined by using perturbation theory as:

$$C_s = C_{s0} + \lambda^x C_{s1},$$

(11)

where $C_{s0}$ is the capacitance of the original homogeneous film (Equation (6)), $C_{s1}$ is the added capacitance due to grading, and $\lambda^x$ is a small parameter ($\ll 1$). In our current work, we assume ($\lambda^x = \lambda = 0.1$) to further simplify our calculations.

First, we grade the relative permittivity $\varepsilon_r$ and elastic constant, $c$, separately. When we grade $\varepsilon_r$ the relation between the coefficients $a$ and $\varepsilon_r$ should be considered. According to Equation (9) and the relation

$$\alpha \varepsilon_0 = (\varepsilon_r - 1)^{-1}$$

we obtain

$$\alpha^{-1} = \alpha_0^{-1} \{1 + \lambda g(x)\} + \varepsilon_0 \lambda g(x).$$

(12)

By substituting Equation (13) into the GE and BC equations (Equations (4)–(5)), we found that the added capacitance due to grading $\varepsilon_r$ only is:

$$C_{s1} = -w \frac{1}{4\alpha_0 A_2 h V_d \eta_0 (h - l \eta_0 + e^{2h/l} (h + l \eta_0))} e^{\frac{h}{l}}$$

$$\left(-4\alpha_0 A_2 h^2 \cosh\left(\frac{h}{l}\right) + 2l(2\alpha_0 A_2 h + V_d (k_1 + k_2 + 2\alpha_0 k_2 \varepsilon_0) \eta_0) \sinh\left(\frac{h}{l}\right) \right)$$

$$+ \alpha_0 B_2 h \left(2h - l \sinh\left(\frac{2h}{l}\right)\right).$$

(14)

The added capacitance due to grading $c$ only is:

$$C_{s1} = -w \frac{B_1 d \varepsilon_0 \eta_0 \left(-2h + l \sinh\left(\frac{2h}{l}\right)\right)}{8l^2 V_d (h \cosh\left(\frac{h}{l}\right) + l \eta_0 \sinh\left(\frac{h}{l}\right))}.$$

(15)

Then, we grade both $c$ ($w = w_1 = -1$) and $\varepsilon_r$ ($w = w_2 = 1$), simultaneously, to obtain
Table 1. Selected parameters and their values for SrTiO$_3$ dielectric film.

| Parameter | Value       | Unit          |
|-----------|-------------|---------------|
| $\varepsilon_r$ | 3.00 x 10$^2$ | unitless      |
| $b$       | 4.14 x 10$^{-6}$ | Nm$^4$/C$^2$ |
| $c$       | 3.5 x 10$^{11}$ | N/m$^2$      |
| $d$       | -1.2 x 10$^2$  | Nm/C         |

$$C_{s1} = \frac{1}{8a_0hl^2V_d\eta_0(h - l\eta_0 + e^{2h/l}(h + l\eta_0))} e^{-\frac{6}{l}} \times \left( -2e^{\frac{h}{l}}(-1 + e^{2h/l})(k_1 + k_2)l^3V_d\eta_0(1 + \eta_0)w_2 \right)$$

$$+ a_0 \left( 4A_2e^{\frac{2h}{l}}hl^2(h + e^{2h/l}(h - l) + l)(1 + \eta_0)w_2 \right)$$

$$+ 2e^{\frac{2h}{l}} \left( -4k_2l^3V_d\varepsilon_0(1 + \eta_0)\sinh \left( \frac{h}{l} \right) w_2 \right)$$

$$+ h(-B_1f\varepsilon_0\eta_0^2w_1 + B_2l^2(1 + \eta_0)w_2 \left( -2h + l\sinh \left( \frac{2h}{l} \right) \right)) \right),$$

where the parameters $B_1$, $B_2$, $B_3$, $A_2$, and $A_3$ are defined [28] as:

$$B_2 = \frac{(1 - k_0)\eta_0V_d}{\left[ \eta_0 \sinh \left( \frac{h}{l} \right) + (\frac{h}{l}) \cosh \left( \frac{h}{l} \right) \right]};$$

$$A_3 = (B_3/\eta_0 l) \cosh (h/l) + k_0V_d/h;$$

$$A_2 = -\varepsilon_0\eta_0A_3; B_2 = \frac{\varepsilon_0B_3}{l} = -\varepsilon_0B_1d;$$

$$k_1 = k_0 = 0.3; k_2 = 1.2k_0 = 0.36$$

The details of solving the partial differential equations (PDEs) can be found in the appendix.

3. Results and discussion

The material constant values used in the calculations of specific capacitance for the 2.7 nm SrTiO$_3$ nanocapacitor are listed in Table 1 [29]. The results of the specific capacitance of uniform and graded dielectric films are tabulated in Table 2. The relationships between the original capacitance $C_{s0}$ and the added capacitance $C_{s1}$ (for three different grading cases) with the longitudinal flexoelectric length scale $l$ and other parameters are shown in Figures 4 and 5.
Table 2. Specific capacitance of uniform and graded dielectric film.

| Capacitance parameter | Graded parameter | Grading direction, W | Specific capacitance (fF µm\(^{-2}\)) | Added capacitance 0.1*Cs1 (fF µm\(^{-2}\)) | Enhancement 0.1*Cs1/Cs0 |
|-----------------------|------------------|----------------------|----------------------------------------|-------------------------------------------|-------------------------|
| Cs0                   | Not graded       | 0                    | 301.65                                 | 0                                         | 0%                      |
| Cs1                   | εr               | 1                    | 320.895                                | 32.09                                     | 11%                     |
| Cs1                   | c                | −1                   | 495.701                                | 49.57                                     | 16%                     |
| Cs1                   | εr & c           | 1 & −1               | 816.596                                | 81.66                                     | 27%                     |

From Figure 4, we notice that the capacitance exhibits linear behavior with respect to the relative permittivity, which can also be verified by inspecting Equations (6), (7) and (12). Since we generally use materials with high relative permittivity (in the order of 10\(^2\) or 10\(^3\)), the constant \(a\) will be several orders of magnitude smaller than \(1/\varepsilon_0\) (Equation (12)) and similarly, the term \(1/\varepsilon_r - 1\) will be several orders smaller than the rest of the summation (Equation (6)). Consequently, changing of \(\varepsilon_r\) does not affect the value of \(l\) and furthermore, the second fraction of Equation (6). Considering the linear grading function \(g(x)\) in the case of \(w = 1\), its range is \([0, 2]\). Therefore, the graded relative permittivity \(\varepsilon_r\) is in the range of \([\varepsilon_{r0}, 1.2\varepsilon_{r0}]\). According to the linear relation shown in Figure 4, the overall capacitance of the dielectric film with graded \(\varepsilon_r\) based on \(\varepsilon_r = 300\) should fall into the range of \([301.65 \text{ fF µm}^{-2}, 360.683 \text{ fF µm}^{-2}]\) which includes our result of 320.895 fF µm\(^{-2}\).

For the case of grading \(c\), we have found a large window of capacitance enhancement. That can be attributed to the high sensitivity of \(l\) with respect to the values of \(b, c\) and \(d\) and
Figure 5. The relations between $C_{s0}$ and $0.1 \times C_{s1}$ (due to grading both $c$ and $\varepsilon_r$) with $\varepsilon_r$, $c$, $b$, and $d$. Thus, its impact on the overall capacitance. Generally, increasing $l$ will lead to reduction in capacitance. We observed a critical value of $l$ around 1 Å below which the curve is very sharp. Above this value ($l = 1$ Å), the curve is nearly flat (slightly decreasing with $l$). There are corresponding critical values of $b$, $c$ and $d$ (Equation (7)). We have found that below those values, the added capacitance becomes unstable, i.e. a slight change in the parameter will result in a very large added capacitance (Figures 4 and 5). Thus, it is recommended to use parametric values above the critical points to remain in the “stable” regions of the $C_{s1}$ curves.

Based on the parametric values we used for the 2.7 nm SrTiO$_3$ nanocapacitor (Table 1), larger capacitance enhancement was achieved by combined grading of $\varepsilon_r$ with $w = 1$ and $c$ with $w = -1$. The results of the original capacitance $C_{s0}$, the added capacitance $0.1 \times C_{s1}$, and the total capacitance $C_s$ of different size nanocapacitors are shown in Figure 6. For $2h = 2.7$ nm, the capacitance enhancement is found to be as large as 27%. Thus, based on our results, grading appears to be an effective method for enhancing capacitance in nanocapacitors.

4. Conclusions

By using perturbation theory, we have calculated the enhancements of capacitance due to grading of selected properties of the dielectric films in parallel-plate nanocapacitors. Combined grading of the relative permittivity $\varepsilon_r$ and the elastic constant $c$ resulted in the enhancement of 27% for the 2.7 nm SrTiO$_3$ nanocapacitors. We also studied the impact of various parameters on the capacitance. Higher $\varepsilon_r$ and lower longitudinal flexoelectric
length scale $l$ will lead to higher capacitance enhancement especially when $l$ reduces to 1 Å. However, the value of $l$ was found to be very sensitive around 1 Å with altering $b$, $c$ and $d$. 

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