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High capacity oxide/ferroelectric/oxide stacks for on-chip charge storage

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A thermodynamic model coupled with an electrostatic analysis of dielectric-ferroelectric-dielectric sandwich structures shows that high capacitance densities can be achieved when the total dielectric thickness reaches a critical fraction. For such cases, the induced polarization in the linear dielectrics (e.g., SiO_2, Ta_2O_5, HfO_2, Al_2O_3, and ZrO_2) increases the overall permittivity until the internal electric field in the ferroelectric layer suppresses the spontaneous polarization of the ferroelectric. Beyond this critical fraction, the ferroelectric layer can no longer induce polarization in the dielectric layers. We specifically determine the critical fraction required for $Ba_{1-x}Sr_xTiO_3$ $(0<x\leqslant 0.2)$ and $Pb_{1-x}Zr_xTiO_3$ $(0<x\leqslant 0.5)$ solid solutions. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2236265]

As the critical dimensions of integrated circuits (ICs) continue to shrink into the nanometer range, it becomes increasingly more difficult for IC manufacturers to use conventional silicon-based materials to form the high capacitance, on-chip elements necessary for dynamic random access memory (DRAM) and filter applications. While a number of nontraditional dielectric (DE) materials have been investigated, including Ta_2O_5, HfO_2, Al_2O_3, ZrO_2, and $Ba_{1-x}Sr_xTiO_3$ (BST), such materials are problematic, not only because their compatibility with convention IC processing must be proven, but also because current deposition means can often produce interface traps, high leakage, and low breakdown strength devices.[1] It is thus highly desirable to maintain as much of the current silicon-based capacitive element structures as possible while increasing their overall storage capacity.

In this study, we consider various dielectric-ferroelectric-dielectric (DE/FE/DE) multilayer structures as replacement elements for the simple DE layers most commonly used in IC processing. Multilayer FE heterostructures are considered as alternative charge storage components because of their extraordinarily high dielectric response.[2] We show that conventional IC dielectrics such as silicon dioxide, silicon nitride, and silicon oxynitride may be incorporated in these structures to produce low leakage and high breakdown strength, while the FE acts to polarize these dielectrics, thereby producing an overall high capacitive structure. We will concentrate on oxide dielectrics although the analysis is equally valid for all linear dielectrics. The theoretical analysis builds upon a previously developed formalism for FE/FE and FE/paraelectric (PE) bilayers and superlattices.[3] This model was employed to explain the gigantic dielectric response in such heterostructures[4,5] and predicts a dielectric anomaly at a critical layer fraction of the PE material at which the dielectric tunability is also maximized.[6] Similar theoretical results regarding the enhancement of the dielectric permittivity were predicted for FE thin films with "dead" layers at the interface with the electrodes.[7]

Consider a DE/FE/DE stack that consists of a FE layer of thickness of h_1 sandwiched between two DE layers of thickness h_2 and h_3 with top and bottom metallic electrodes, as shown in Fig. 1. The dielectric layer can be any low-loss dielectric material, such as SiO_2, Si_3N_4, or HfO_2.[8] We will assume for simplicity that the trilayer is symmetric, i.e., the DE layers have the same thickness $h_2=h_3$. The total energy density of this configuration can be written as

$$F_{\Sigma}=(1-2\alpha)\left[F_1(P_1)-\frac{1}{2}E_{D,1}P_1-EP_1\right]+2\alpha\left[F_2(P_2)-\frac{1}{2}E_{D,2}P_2-EP_2\right]+\frac{F_S}{h}, \qquad (1)$$

where $\alpha=h_2/h$ is the relative thickness of the DE layer, $h=h_1+2h_2$ is the total thickness of the multilayer heterostructure, P_1 and P_2 are the polarizations the FE and DE layers, respectively, and E is an applied electric field parallel to the polarization. $E_{D,1}$ and $E_{D,2}$ are the internal fields in the layers that arise from the interlayer polarization mismatch.[3] The last term F_S is the sum of the surface energies of the interlayer interfaces that contain the contribution by the interface defect structures and traps. This surface energy can be neglected if the individual layers are sufficiently thick, of the order of 10 nm,[3] since the strength of the electrostatic and elastic fields of the interface diminishes rapidly away from interface.[9]

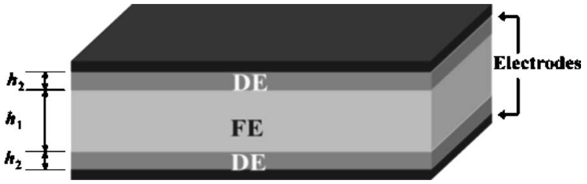

FIG. 1. A freestanding DE/FE/DE stack sandwiched between metallic electrodes. The thicknesses of the FE and DE layers are h_1 and h_2, respectively.

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In Eq. (1), $F_1(P_1)$ is the free energy density of the FE layer that can be expressed as a Landau expansion, such that

$$F_1(P_1) = F_{0,1} + \frac{1}{2}a_1P_1^2 + \frac{1}{4}b_1P_1^4 + \frac{1}{6}c_1P_1^6, \qquad (2)$$

where $F_{0,1}$ is the free energy of the FE in the PE state and a_1, b_1, and c_1, are the Landau coefficients of bulk FE. The temperature dependence of the dielectric stiffness a_1 is given through the Curie-Weiss law, $a_1=(T-T_C)/\varepsilon_0 C$, where ε_0 is the permittivity of free space and T_C and C are the Curie-Weiss temperature and constant of FE layer. The other Landau expansion coefficients are assumed to be temperature independent. For a linear DE, the free energy $F_2(P_2)$ of the DE layers is given by

$$F_2(P_2) = \frac{1}{2}a_2P_2^2 = \frac{1}{2\varepsilon_0\varepsilon_R}P_2^2, \qquad (3)$$

where a_2 and ε_R are the (uncoupled) dielectric stiffness and relative dielectric constant of the DE, respectively.

The spontaneous polarization of the layers in their uncoupled state $(P_{0,i})$ follows from the condition of thermodynamic equilibrium, $\partial F_i/\partial P_i=0$, such that

$$P_{0,1}^2 = \frac{-b_1+\sqrt{b_1^2-4a_1c_1}}{2c_1}, \quad P_{0,2}^2=0. \qquad (4)$$

We note that the internal stresses that might arise from the lattice misfit in heteroepitaxial stacks or the thermal expansion mismatch can be incorporated into the free energy densities via the renormalized Landau coefficients.[10,11] For the sake of simplicity, we will assume in this study that the layers are completely relaxed and the trilayer structure is not clamped by a thick substrate.

The actual polarization of the layers in the DE/FE/DE stack should obviously differ from $P_{0,i}$ because of the electrostatic interaction between the layers due to the internal electric fields $E_{D,1}$ and $E_{D,2}$. For perfectly insulating bilayers,[3,12]

$$E_{D,1} = -\frac{1}{\varepsilon_0}(P_1-\langle P\rangle) = \frac{2\alpha}{\varepsilon_0}(P_2-P_1), \qquad (5)$$

$$E_{D,2} = -\frac{1}{\varepsilon_0}(P_2-\langle P\rangle) = \frac{1-2\alpha}{\varepsilon_0}(P_1-P_2), \qquad (6)$$

where $\langle P\rangle=(1-2\alpha)P_1+2\alpha P_2$ is the average polarization. $E_{D,2}$ induces polarization in the DE layers, whereas $E_{D,1}$ attempts to decrease the polarization of FE layer as to minimize the initial polarization difference, $\Delta P=P_{0,1}$. The polarization in each layer is given by the simultaneous solution of equations of state, $\partial F_\Sigma/\partial P_i=0$. It is expected that $P_{C,1}<P_{0,1}$ and $P_{C,2}>0$ in the trilayer, where $P_{C,1}$ and $P_{C,2}$ are the equilibrium polarizations in the FE and DE layers, respectively, and correspond to the solutions of $\partial F_\Sigma/\partial P_i=0$.

The (small-signal) average dielectric response of the DE/FE/DE heterostructure along the direction of the polarization is

$$\langle\varepsilon_R\rangle \cong \frac{1}{\varepsilon_0}\frac{\partial\langle P_C\rangle}{\partial E} = \frac{1}{\varepsilon_0}\left[(1-2\alpha)\frac{\delta P_{C,1}}{E}+2\alpha\frac{\delta P_{C,2}}{E}\right], \qquad (7)$$

where $\langle P_C\rangle=(1-2\alpha)P_{C,1}+2\alpha P_{C,2}$ is the equilibrium average polarization of the stack and $\delta P_{C,i}=P_{C,i}(E)-P_{C,i}(E=0)$ as $E\rightarrow 0$. The average dielectric constant of the trilayer is expected to increase substantially at a critical DE fraction similar to FE/PE bilayers as the dielectric layer polarizes to ever larger values.[3] This behavior resembles the λ-type anomaly near a phase transformation. The reason for this behavior is that for larger fractions of the DE layer, $E_{D,1}$ completely suppresses ferroelectricity in the FE layer. Beyond this critical fraction, the FE layer can no longer induce polarization in the DE layers.

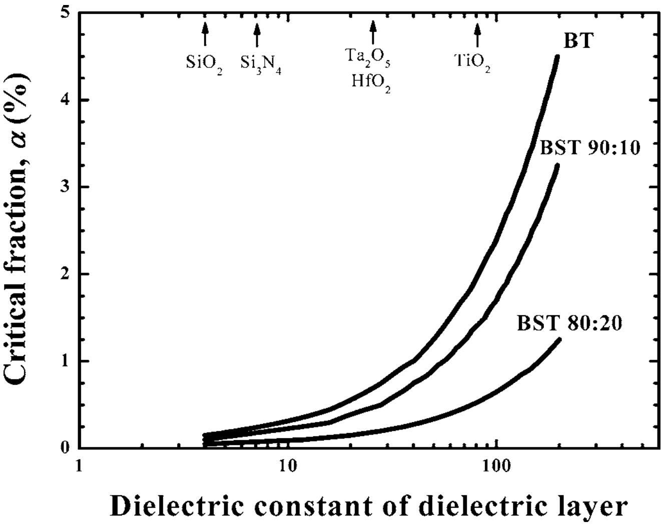

FIG. 2. Critical fraction of DE/BST/DE stacks as a function of the (bulk) dielectric constant of DE layer. Results for BaTiO$_3$ (BT), Ba$_{0.9}$Sr$_{0.1}$TiO$_3$ (BST 90:10), and Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ (BST 80:20) as the FE layers are shown.

In this study, we consider two materials systems as the FE layer: Ba$_{1-x}$Sr$_x$TiO$_3$ (BST) with $0\leqslant x\leqslant 0.2$ and Pb$_{1-x}$Zr$_x$TiO$_3$ (PZT) with $0\leqslant x\leqslant 0.5$. In the specified composition range, these FE materials have the prototypical perovskite lattice, which transforms from the PE cubic to FE tetragonal crystal structure upon cooling, and are FE at room temperature (RT) at which the calculations were carried out. The thermodynamic parameters and the Landau coefficients of these materials are well known[13,14] which allows us to perform a numerical analysis to determine the dielectric response of a DE/FE/DE stack. The polarization in each layer is calculated from the condition of thermodynamic equilibrium $\partial F_\Sigma/\partial P_i=0$ and the dielectric response is determined from Eq. (7).

A series of calculations was carried out to determine the critical fraction of the DE layer where the gigantic average dielectric response is expected for BST and PZT stacks as a function of the uncoupled (or bulk permittivity) ε_R of the DE layer. These results are plotted in Figs. 2 and 3. As an example, in a SiO$_2$/Ba$_{0.8}$Sr$_{0.2}$TiO$_3$/SiO$_2$ stack, where SiO$_2$ is a typical gate material with $\varepsilon_R=4$, the anomaly in $\langle\varepsilon_R\rangle$ of the trilayer is around 0.05%. A SiO$_2$/BT/SiO$_2$ trilayer shows a higher critical fraction, ~0.15%, compared to the BST stack. This is because BT has a higher initial polarization, and thus there is a larger initial polarization difference between the FE and the DE. Likewise, the critical fractions in SiO$_2$/PZT/SiO$_2$ are higher than those in SiO$_2$/BST/SiO$_2$ stacks (Fig. 3). Furthermore, it is clear from Figs. 2 and 3 that the larger the bulk ε_R of the DE, the larger the critical fraction will be due to a higher induced polarization by the internal electrical field in the DE. We also mark in these plots the bulk ε_R of typical linear DEs (Ref. 8) to provide an estimate

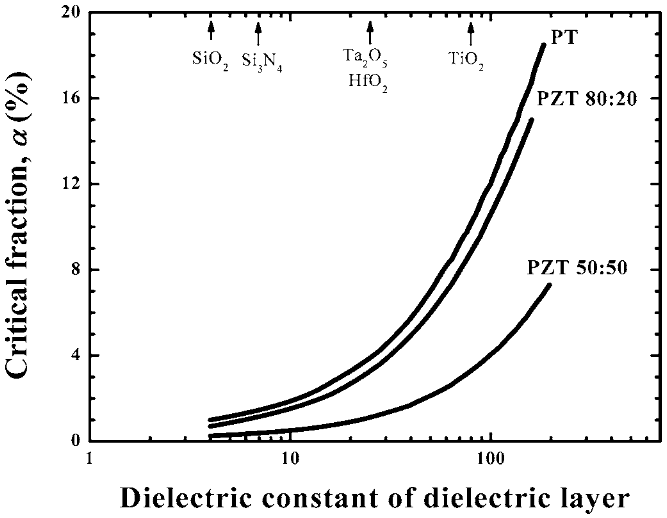

FIG. 3. Critical fraction of DE/PZT/DE stacks as a function of the dielectric constant of DE layer. Results for $PbTiO_3$ (PT), $Pb_{0.8}Zr_{0.2}TiO_3$ (PZT 80:20), and $Pb_{0.5}Zr_{0.5}TiO_3$ (PZT 50:50) as the FE layers are shown.

as to where the critical layer fraction is expected for the maximum dielectric response.

In addition to the obvious advantage of higher charge storage capabilities due to the extremely high dielectric response, another technologically important implication of oxide/FE heterostructures is that they offer an efficient way to reduce dielectric loss and leakage. The DE oxide serves as a buffer between the FE and the metallic electrodes. The elimination of these metal-FE interfaces would significantly reduce charge injection from the metal into the FE or leakage of charges from the FE into the metal that results in deterioration in the dielectric properties of simple FE capacitors. This has been one of the long-standing problems that have prevented the use of high dielectric constant FEs such as BST in charge storage applications. Indeed, low dielectric losses have been reported experimentally in BST films on SiO_2, Ti–Al, and Teflon buffer layers.[15–17] Furthermore, the concepts developed here also imply that multiple oxide/FE stacks with a systematic variation in the FE layer composition would result in a heterostructure with a high dielectric response that remains constant over a relatively large temperature range.

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