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Interface-related thickness dependence of the tunability in $BaSrTiO_3$ thin films

U. Ellerkmann,[a] R. Liedtke, and U. Boettger
Institut für Werkstoffe der Elektrotechnik, RWTH Aachen, D-52056 Aachen, Germany

R. Waser
Institut für Werkstoffe der Elektrotechnik, RWTH Aachen, D-52056 Aachen, Germany and Elektrokeramische Materialen, Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

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The thickness dependence of the tunability of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films is investigated. The capacitance–voltage curves, revealing the tunability of the films with thickness from 30 to 370 nm, show a strong thickness dependence. This is attributed to a bias-independent interface capacity. The interface suppresses the permittivity of the film with increasing influence for decreasing film thickness, whereas the tunability of the bulk of the film remains constant. Calculations are performed from a thermodynamic model based on the Landau–Ginzburg–Devonshire theory leading to the assumption of the bias-independent interface capacity. The bias dependence of the bulk of the films derived from measurement data are in very good agreement with the theoretically derived values. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1824173]

Perovskite thin films such as $Pb(Zi_xTi_{1-x})O_3$ and $(Ba_xSr_{1-x})TiO_3$ (BST) are currently of high interest and under intense investigation for applications as storage devices such as ferroelectric random access memory,[1,2] high permittivity dielectrics in high density dynamic random access memories,[3,4] as well as tunable microwave devices such as phase shifters[5,6] and filters.[7] In the course of miniaturization a suppression of the dielectric constant with decreasing film thickness has been observed.[8,9] Intense investigations on this topic have shown an interface capacity to be responsible for this effect. Despite experimental proof of the existence of the interface capacity, its physical origin is unknown and under discussion. Possible physical origins are the existence of low dielectric interface regions caused by strain due to different thermal expansion coefficients of substrate, electrode, and perovskite thin film,[10] accumulation of oxygen vacancies at the electrodes,[11] local diffusion of electrode material into the film,[12,13] and formation of surface states.[14] Also a field penetration into the electrode is discussed[15–17] and depolarization fields due to incomplete screening by the electrodes.[18,19] For columnar films a dead layer at the grain boundaries, though resulting in a set of parallel capacitors, has also been shown to be able to explain the observed phenomena.[20] This work will focus on the influence of the interface effect on the tunability of thin films. One important aspect in the course of this investigation is the bias dependence of the interface capacitance in order to separate interface capacity and bulk effects from the total measured effective capacity.

A set of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films was deposited on standard $Si/SiO_2/Ti/Pt$ wafers with film thickness from 30 to 370 nm using the chemical solution deposition method.[21] Details about sample preparation have been reported earlier.[9] Dielectric measurements were performed with a HP 4284 precision LCR meter at room temperature to determine the tunability of the films. Additional zero bias dielectric measurements were performed at temperatures from 20 to 550 K controlled by an MMR Technologies measurement setup.[9] SEM images revealed dense films with columnar structures for all films.

It has been reported before that the permittivity of BST thin films is strongly dependent on the thickness of the BST film for low bias voltage whereas the permittivity of the films is almost thickness independent for high applied fields.[22] In this contribution we will investigate whether this can be attributed to a bias dependence of the interface capacity or whether this is the expected behavior for a thin film with no or at least bias-independent interface capacity. Figure 1 shows the bias dependence of the effective permittivity for different film thicknesses. Now it is interesting to separate the interface and bulk capacity to look at the thickness dependence of the bulk of the films. According to the series capacitor model the reciprocal capacitance density depends linearly on the film thickness. From the slope and the nonzero *y*-axis intercept of the linear fit the permittivity and the interface capacity can be extracted. In Fig. 2 the inverse capacitance density versus film thickness is shown for selected applied bias voltages. If the above-mentioned linear fit would be applied to the measurement points it can be clearly seen that for the smallest film thicknesses the measurement points deviate to smaller values than given by a linear fit. This deviation becomes larger for further decreasing film thickness. Therefore it is questionable if a linear fit is still justi-

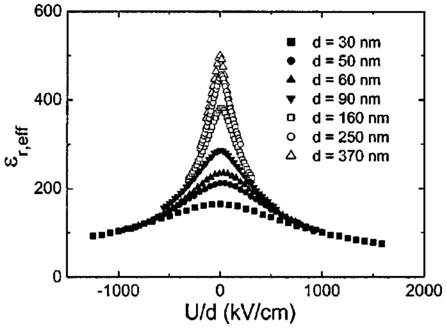

FIG. 1. Effective relative dielectric constant vs applied dc electric field, derived from capacitance–voltage measurements for the $Pt/BST(70/30)/Pt/Ti/SiO_2/Si$ samples with BST film thicknesses of 30–370 nm.

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[a] Electronic mail: ellerkmann@iwe.rwth-aachen.de

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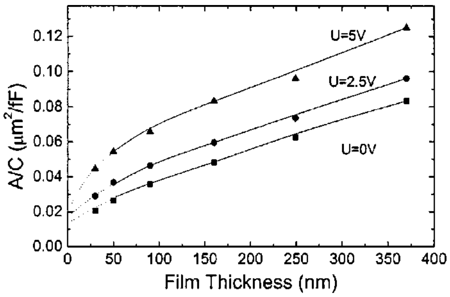

FIG. 2. Inverse capacitance density vs film thickness for different applied dc bias voltages. The dotted line indicates a possible run of the curve for small film thicknesses.

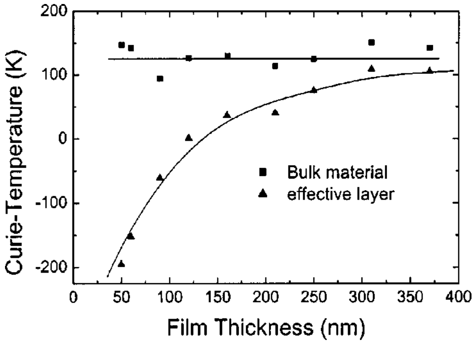

FIG. 3. Curie temperature of the measured effective dielectric constant (▲) and the bulk dielectric constant (■) (with the interface subtracted from the measured values) as a function of film thickness derived from $\varepsilon(T)$ measurements.[9]

fied. The true behavior could also be as indicated by the dotted line for small thicknesses in Fig. 2. For the further procedure it has to be analyzed what behavior would be expected from the theory and an expression of the permittivity as a function of the applied field is to be found.

From the derivative of the thermodynamic potential $\tilde{G}$ the dependence of the polarization of the applied field is given in the following:[10,23,24]

$$\frac{\partial \tilde{G}}{\partial P_1} = 2(\alpha_1^* + \alpha_{13}^* P_3^2 + \alpha_{12}^* P_2^2)P_1 + 4\alpha_{11}^* P_1^3 - E_1 = 0, \quad (1)$$

$$\frac{\partial \tilde{G}}{\partial P_2} = 2(\alpha_1^* + \alpha_{13}^* P_3^2 + \alpha_{12}^* P_1^2)P_2 + 4\alpha_{11}^* P_2^3 - E_2 = 0, \quad (2)$$

$$\frac{\partial \tilde{G}}{\partial P_3} = 2(\alpha_3^* + \alpha_{13}^* (P_1^2 + P_2^2))P_3 + 4\alpha_{33}^* P_3^3 - E_3 = 0, \quad (3)$$

where P_1, E_1 and P_2, E_2 are the in-plane components of the polarization and applied field, respectively, P_3 and E_3 are the out-of-plane components of the polarization and field, respectively, and α_i^*, α_{ij}^* are the renormalized expansion coefficients. For the films under investigation it has been shown that at room temperature the films are in the paraelectric phase[9] and therefore have a cubic cell structure. This means that we do not have a spontaneous polarization in any room direction and at zero bias $P_1 = P_2 = P_3 = 0$.[10,24] Additionally the field is only applied in the out-of-plane direction resulting in an induced polarization in this direction (P_3) so that for the further consideration only Eq. (3) has to be evaluated. The dependence of the relative dielectric constant on the applied electric field can be determined by differentiating Eq. (3). Consideration of the components of the polarization leaves us with two equations:

$$\begin{aligned}\frac{\varepsilon_{33}(E_3)}{\varepsilon_0} &= \left(\varepsilon_0 \frac{\partial^2 \tilde{G}}{\partial P_3^2}\right)^{-1} \\ &= \frac{1}{2\varepsilon_0(\alpha_3^* + \alpha_{13}^*(P_1^2 + P_2^2) + 6\alpha_{33}^* P_3^2)} \\ &= \frac{1}{2\varepsilon_0(\alpha_3^* + 6\alpha_{33}^* P_3^2)}, \end{aligned} \quad (4)$$

$$\frac{\partial \tilde{G}}{\partial P_3} = 2\alpha_3^* P_3 + 4\alpha_{33}^* P_3^3 - E_3 = 0. \quad (5)$$

The renormalized coefficients α_3^*, α_{33}^* of the free energy expansion are given by

$$\alpha_3^* = \alpha_1 - u_m \frac{2Q_{12}}{s_{11} + s_{12}}, \quad \alpha_{33}^* = \alpha_{11} + \frac{Q_{12}^2}{s_{11} + s_{12}}, \quad (6)$$

where α_1 is the dielectric stiffness, α_{11} is the higher order stiffness coefficient at constant stress, Q_{12} is the electrostrictive coefficient, u_m is the misfit strain, and s_{11} and s_{12} the elastic compliances. The dielectric stiffness is given by the Curie–Weiss law, $\alpha_1 = (T - T_0)/2\varepsilon_0 C$, where T_0 and C are the Curie temperature and constant, respectively, of a bulk film. In Eq. (4) the dielectric constant is given as a function of the polarization and in Eq. (5) the applied field is given as a function of the polarization. With a numerical solution this gives us the desired dielectric constant as a function of the applied field. Alternatively Eq. (5) can be inverted giving the polarization as a function of the applied field. By further differentiating a closed form for $\varepsilon = f(E)$ has been derived by Streiffer *et al.*[25] A simpler form has been found earlier by Johnson as a description of this behavior.[26] This form has been found to fit the behavior fairly well for a limited field range. For a larger field range a parameter has to be inserted and adjusted for different regions or used as a free parameter.[25,27]

Now, for plotting the permittivity as a function of the applied field, the parameters from Eq. (6) have to be calculated using the material parameters for bulk films. However, to determine the α_3^* coefficient, the misfit strain has to be known. Also the misfit strain strongly effects the Curie parameters of the film,[28,29] which are needed to determine the dielectric stiffness α_1. To get a value describing the behavior of the films under investigation more precisely the α_3^* coefficient may be determined by using experimental data to extract the values of the Curie constant. α_3^* is then given by $\alpha_3^* = (T - T_0)/2\varepsilon_0 C$ with T_0 and C being the Curie parameters of the film from experimental data. It should be noted that the calculation of the tunability is not affected by this method since the Curie parameters are extracted from zero bias measurements and do not affect the tunability.

The Curie parameters were extracted from temperature-dependent measurement of the zero bias dielectric constant in a temperature range from 20 to 550 K.[9] The result for the Curie temperature of the effective layer as a function of the film thickness is shown in Fig. 3 (triangular symbols). It shows that the Curie temperature is strongly dependent on the film thickness. To extract the bulk value, the interface can be subtracted from the measured effective dielectric constant leaving the bulk dielectric constant. Therefore the temperature dependence of the interface capacitance was determined

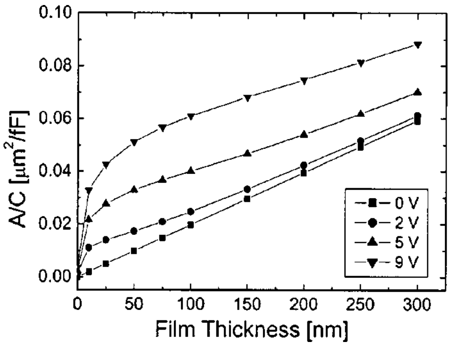

FIG. 4. Inverse capacitance density as a function of film thickness for different applied biases calculated from the phenomenological model. Clearly, a linear fit is not justified (see also Fig. 2).

and found to be independent of the temperature for the films under investigation in the measured temperature range.[9] The Curie temperature for the bulk can be derived (Fig. 3) and is shown to be independent of the film thickness. The Curie constant C is also found to be thickness independent and is not affected by the interface capacity (not shown here).

To calculate the renormalized coefficients of the free energy expansion the Curie parameters were determined to be $T_0=125$ K (see also Fig. 3) and $C=10^5$ K. The material coefficients of the film composition under examination are taken from literature values[30] and are $\alpha_{11}=1.767\times 10^8\ \mathrm{m^5/C^2F}$, $s_{11}=5.9\times 10^{-12}\ \mathrm{m^2/N}$, $s_{12}=-1.9\times 10^{-12}\ \mathrm{m^2/N}$, and $Q_{12}=-0.0346\ \mathrm{m^4/C^2}$ (calculated by linear interpolation of the $BaTiO_3$ and $SrTiO_3$ parameters). With these data the bias dependence of the inverse capacitance density versus thickness behavior can be calculated and is shown in Fig. 4. It clearly shows that a linear fit is not justified and the observed behavior in Fig. 2 cannot be attributed to a bias-dependent interface capacity. In fact the experimental data show approximately the behavior expected from theory with no or with a bias-independent interface capacity. The small deviance can be explained by the fact that the elastic compliances s_{ij} are not known with high accuracy. Yet the curve is very sensitive to these values. A small change in the supposed values would lead to even better fits.

From the measured dielectric constant of the effective layer structure the interface can now be subtracted leaving the bulk behavior of the film for different film thicknesses. The result is shown in Fig. 5. It shows an almost thickness-independent tunability of the bulk of the film. Furthermore the continuous line gives the theoretic value with the given material parameters and shows a very good agreement with the experimental data.

In summary, the thickness dependence of the tunability has been attributed to a bias-independent interface capacity. Calculations from a thermodynamic model based on the LGD phenomenology have shown that the inverse capacitance density over film thickness plot cannot be fitted by a straight line if a nonzero bias is applied. An extrapolation to the nonzero intercept to determine the interface capacity is therefore not possible. Measurement data show the same behavior as calculations based on theoretical backgrounds predict. The determined tunability of the bulk of the film (with the interface subtracted from the measured data) are in very good agreement with the theoretical values

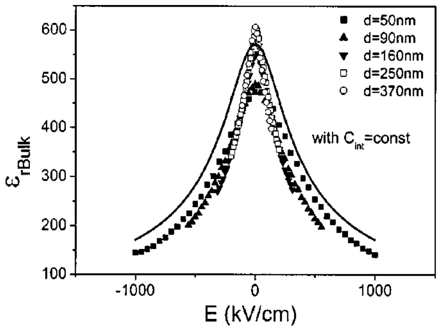

FIG. 5. Tunability of the bulk of the films with the interface capacity subtracted from the measured effective dielectric constant for different film thicknesses. The continuous line is the result of the calculated tunability using the phenomenological model. Experiment and theory are in good agreement.

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