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Scaling Effect on the Dielectric Constant in $Ba(Ti_xZr_{1-x})O_3$ Thin Films

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Abstract. Recent work on PZT and BST thin films reveal a thickness dependence of the dielectric constant for a film thickness below 100 nm. This effect is commonly attributed to an interfacial layer between the electrode and the dielectric film (dead layer). In this contribution we report on the influence of the film thickness on the dielectric constant of $Ba(Ti_xZr_{1-x})O_3$ thin films with different Zr-contents ($x = 0$–30 at.%). The films were prepared by chemical solution deposition (CSD) with thickness between 30 and 350 nm.

The electrical characterization was performed in a temperature range between 25 and 200°C. Results were interpreted with respect to the formation of a serial dead layer capacitance.

Keywords: dielectric properties, $Ba(Ti_xZr_{1-x})O_3$, interface capacitance

Introduction

Compared to the bulk dielectric properties, the thin films show a different behavior like decreasing permittivity with decreasing film thickness. Different theories have been used to explain this phenomenon [1]. The one we chose in this contribution is the existence of an interfacial layer between the electrode and the bulk material. As shown in Fig. 1, an equivalent circuit can be used to describe the whole structure. For the bulk material a RC-parallel cell is used, for the interface layer there are two capacitors in series with the RC cell.

Following Eq. (1), the elements of the circuit diagram can be determined, where A stands for the area, $C_{\text{eff}}/\varepsilon_{\text{eff}}$, C_i/ε_i, and $C_{\text{bulk}}/\varepsilon_{\text{bulk}}$ stand for the effective capacitance/permittivity of the complete structure, the interface capacitance/permittivity and the bulk capacitance of the material, respectively. The total thickness of the film is d and δ the thickness of the two interfacial layers.

$$\frac{A}{C_{\text{eff}}} = \frac{A}{C_i} + \frac{A}{C_{\text{bulk}}} = \frac{\delta}{\varepsilon_i \varepsilon_0} + \frac{d-\delta}{\varepsilon_{\text{bulk}}\varepsilon_0} \qquad (1)$$

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As it cannot be defined whether the influence comes from the upper or lower interface capacitance the two are combined as one. The interface permittivity and the thickness of the interface layer cannot be determined separately, only the quotient of δ/ε_i.

Sample Preparation and Measurement Procedure

For this contribution BTZ thin films with Zr-contents between 0 at.% and 30 at.% were prepared by using a CSD route with barium acetate, titanium *n*-butoxoide and zirconium *n*-propoxide. The samples also were doped with a dose of 1 at.% Mn. In the ceramic samples the Mn was used to lower the leakage current. To get a better comparability for thin films and bulk ceramics, the composition of the thin films also contained 1 at.% Mn. The precursor solution was deposited on a platinum coated Si-wafer by spin coating, and then annealed at 750°C in an oxygen atmosphere. This was repeated for multiple layers until the desired thickness was achieved. The thicknesses of the films range between 30 and 350 nm. Defects that occurred during the sputtering process of the top electrode were healed

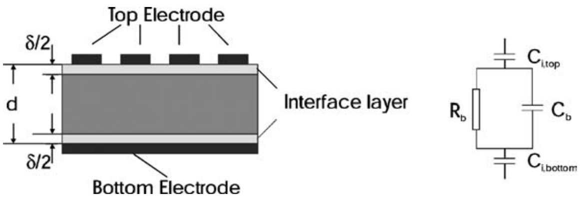

Fig. 1. Schematic of the total structure and circuit diagram.

out in a last annealing step at 550°C for 30 min in oxygen.

To receive results about the dielectric behavior the capacitance measurements in dependence of the temperature were performed using an HP 4194 A impedance analyzer. The frequency was 10 kHz at an amplitude of 30 mV, while the temperature ranged between room temperature and 550 K

Results

To receive the value for the interface capacitance we plotted the inverse capacitance density in dependence of the film thickness. Assuming that the thickness of the material layer is much thicker than for the interface layer, the thickness of the interface layer can be neglected. Extrapolation of the capacitance density to zero film thickness leads to the interface capacitance. As shown in Fig. 2, these values differ with the Zr-content. Below Zr-contents of 18 at.%, the interface capacitance nearly is independent from the temperature, for higher contents it starts decreasing with increasing temperature.

McAneney et al. [2] also found a temperature dependence for the interfacial capacitance in barium strontium titanate capacitors. A possible explanation for this

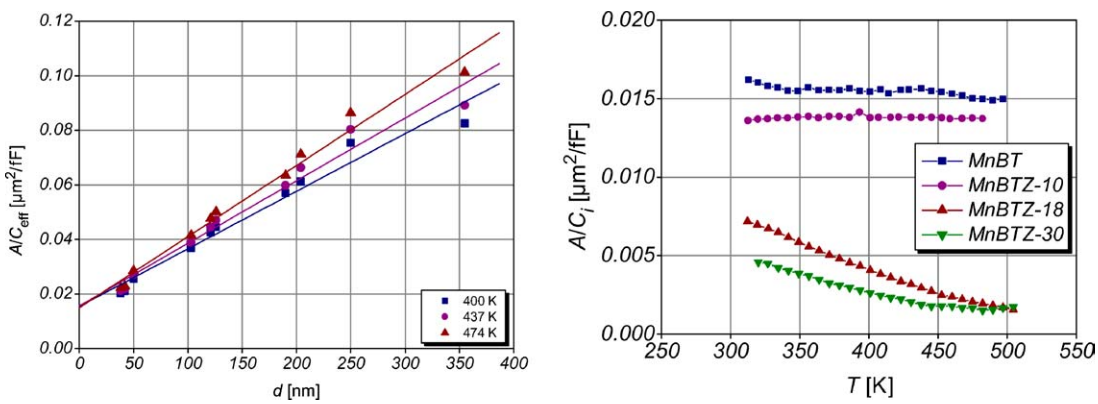

Fig. 2. A/C_{eff} in dependence of film thickness and A/C_i in dependence of temperature.

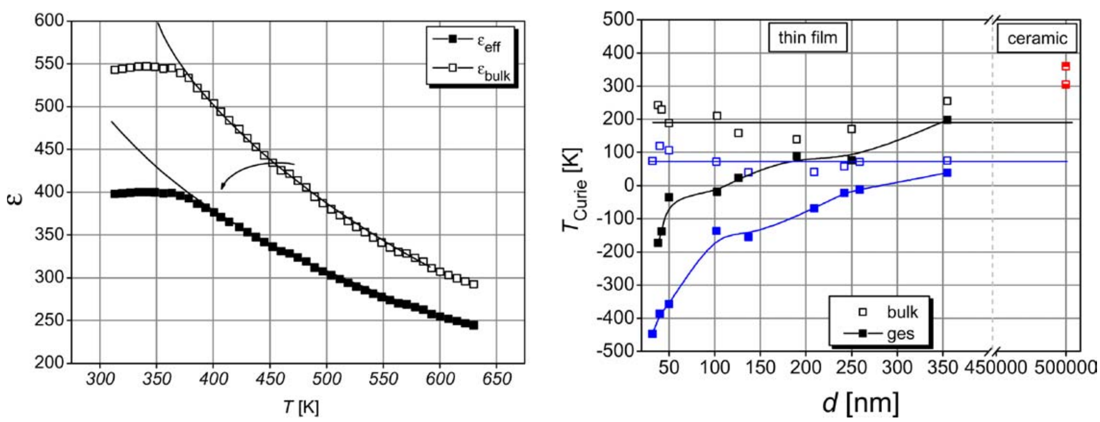

Fig. 3. Bulk and effective permittivity of a 204 nm MnBT sample and Curie temperature for bulk and effective capacitance for MnBT and MnBTZ-10.

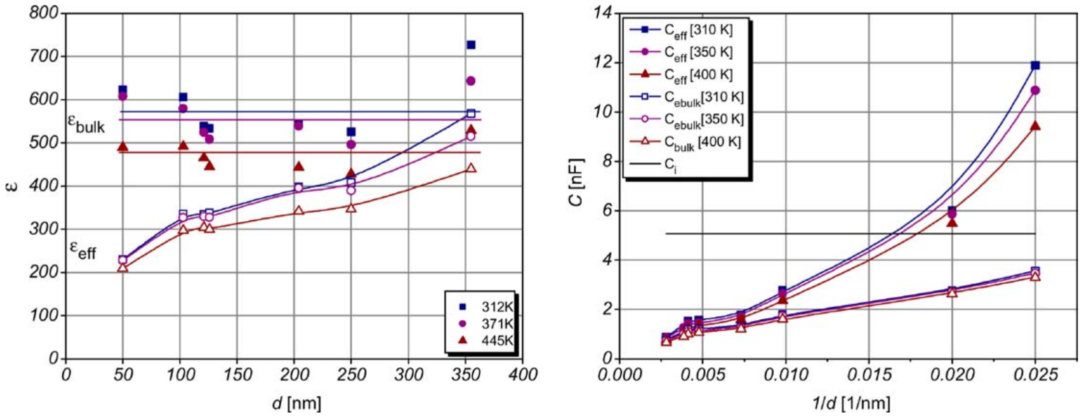

Fig. 4. Effective permittivity and bulk permittivity for MnBT and influence of interface capacitance on the effective capacitance.

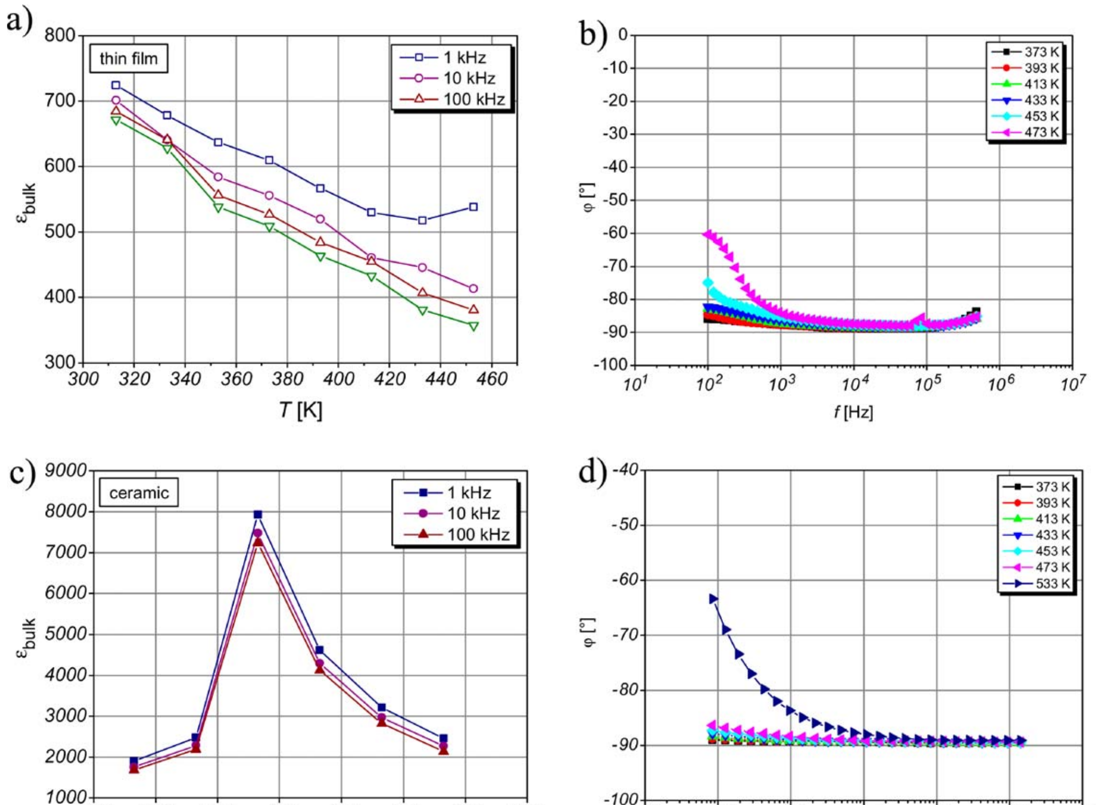

Fig. 5. Bulk permittivity for thin films (a) and for ceramics (c) in dependence of temperature and phase for thin films (b) and ceramics (d) in dependence of frequency.

behavior of the BTZ samples might be that substrate and material have different thermal expansion coefficients, and that these coefficients depend on the Zr content. Another reason might be the mechanical stress between Pt electrode and the material as found Abe et al. for BST films [3]. To get information about the influence of the interface capacitance on the temperature behavior the bulk capacitance was calculated from the measurements by subtracting the interface capacitance. For these results we see, that the bulk permittivity $\varepsilon_{\text{bulk}}$ is much higher than the effective permittivity ε_{eff} of the total thin film (see Fig. 3). By Extrapolation of the $1/\varepsilon$ plot over temperature we received the Curie temperatures for bulk and effective capacitances. These values are more than 120°C lower than for 500 μm thick bulk ceramics (T_{Curie} values for ceramics from [4]). Also it can be seen that the Curie temperature for the bulk of the thin film rather is independent from temperature compared to the one of effective capacitance.

Similar effects of the film thickness on the permittivity for BST/PZT thin films had been previously reported [5]. Different reasons for this behaviour have been discussed in [1]. Figure 4 shows the effective and the bulk permittivity over the film thickness. As can be seen, with increasing film thickness the effective permittivity also increases, but is always lower than the bulk permittivity.

The bulk permittivity seems to be independent from the film thickness. So it seems that the interface layer limits the effective permittivity and thus the effective capacitance. Hence, the maximum effective capacitance to be obtained is the interface capacitance. This is elucidated in a C over inverse film thickness plot in Fig. 4.

For BST thin films the bulk capacitance follows a $1/d$ dependence in contrast to the samples presented here [5].

In Fig. 5 a comparison of $\varepsilon_{\text{bulk}}$ and φ of ceramics and thin films is shown. In the presented temperature range the $\varepsilon_{\text{bulk}}$ of the thin film decreases with increasing temperature whereas the $\varepsilon_{\text{bulk}}$ of the ceramic shows a maximum. As also can be seen the influence of the bulk resistance R_{b} starts for lower temperatures in thin films.

Conclusion

In this contribution we revealed that the interface capacitance is nearly independent of temperature only for Zr-contents <18 at.% and that T_{Curie} is influenced by changes of the film thickness due to the interface effect. The effective film capacitance is limited by the interface capacitance and cannot be increased by a further decrease of the film thickness.

It was also shown that the influence of the bulk resistance on the impedance starts at lower temperatures for thin films in comparison to bulk ceramics and that the T_{Curie} of bulk ceramics is around 120°C higher than T_{Curie} of thin films.

References

1. R. Waser, *Integrated Ferroelectrics*, **15**, 39 (1996) and references therein.
2. J. McAneney, *Journal of Applied Physics*, **94**(7), 4566 (2003).
3. K. Abe, *Japanese Journal of Applied Physics*, **33**, 5297 (1994).
4. C. Hofer, *Journal of the European Ceramic Society* (in press).
5. U. Ellerkmann, *Ferroelectrics*, **271**, 315 (2002).