Change in the ferroelectric to paraelectric phase transition order in P(VDF-TrFE) copolymer ultra-thin films

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Abstract: Dielectric non-linearities in P(VDF-TrFE) ferroelectric thin films were measured in order to prove a thickness dependent change in the ferroelectric to paraelectric phase transition order. The relation between the second order non-linear permittivity ε_3 and the second Landau parameter γ was used to derive the type of transition present in the thin films. It has been found, that the change in the sign of ε_3 for a 30 nm thin film possibly indicates a change in the Curie transition from 2nd to 1st order.

Keywords: Ferroelectrics, Phase Transition, P(VDF-TrFE), Thin Films

Introduction

Due to their unique properties, thin films of ferroelectric materials have drawn increasing attention during the last years. They can be used in numerous applications, e.g. in thin film ferroelectric field effect transistors for non-volatile memory storage. It is well known, that the minimisation of thickness below a certain limit leads to a change in properties, i.e. in ultra-thin films. One of the key properties of a ferroelectric material is the order of Curie transition it undergoes.

Results and Discussion

As published earlier [1], the higher order non-linear permittivities in the paraelectric phase can be related to the Landau parameters. By using the equations for the free energy *F* and the dielectric displacement *D*:

$$F = F_0 + \frac{\alpha}{2} D^2 + \frac{\gamma}{4} D^4 + \frac{\delta}{6} D^6 - ED$$

$$D = P_S + \varepsilon_0 \varepsilon_1 E + \varepsilon_0 \varepsilon_2 E^2 + \cdots$$

it can be derived, that in the paraelectric phase the Landau parameter γ and the permittivity ε_3 are related in the following way:

$$\varepsilon_0 \varepsilon_3 = -\gamma / \alpha^4.$$

Furthermore, the type of phase transition is determined by the sign of the second Landau parameter γ. While a negative sign indicates a first order phase transition, a positive sign will be assigned to a second order phase transition. As can be seen from the relation above, for ε_3 the opposite is true. *Qu* et al. [2] have suggested a change of the transition order for thin films, while *Ong* et al. [3] have concluded otherwise.

While our approach is of different nature, Figure 1 clearly indicates an alternation of the sign of ε_3 in the paraelectric phase if decreasing the thicknesses of the film. In the paraelectric phase we generally observe a negative ε_3 for films thicker than 100 nm indicating a second order transition. If the thickness is decreased to 30 nm, ε_3 stays positive after the ferroelectric to paraelectric phase transition.

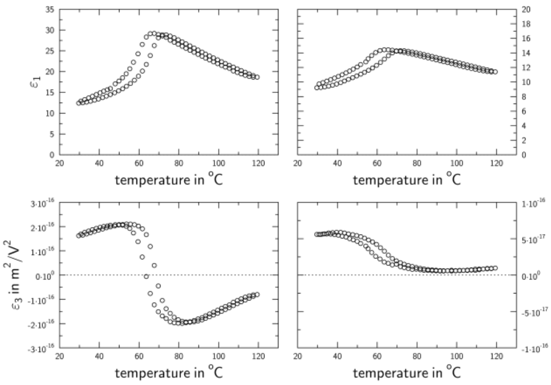

Figure 1: Permittivities ε_1 and ε_3 for a 130 nm thick (left) and a 30 nm (right) thick P(VDF-TrFE) thin film.

Conclusions

It has been shown, that reducing the thickness of P(VDF-TrFE) ferroelectric thin films with molar ratio 56/44 causes a change in the sign of the second order non-linear permittivity ε_3. Using the equations derived earlier, this alternation indicates a change in the ferroelectric to paraelectric phase transition from second to first order.

References

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