Nonlinear Dielectric Properties and Polarization in Thin Ferroelectric P(VDF-TrFE) Copolymer Films

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ABSTRACT

Thin VDF-TrFE copolymer films of molar composition 70/30 and thickness from 25 nm to 175 nm have been prepared by spin coating on a glass substrate covered with an aluminum electrode. The linear, second and third order permittivities ε_1, ε_2 and ε_3 of poled and unpoled samples have been studied versus temperature in heating and cooling cycles up to 120 °C, i.e., above the Curie temperature. The polarization and its temperature dependence are derived from ε_1 and ε_2. This allows a non-destructive readout of the polarization state. It is found that above the Curie temperature and after cooling to room temperature a non-switchable polarization remains. This non-switchable polarization points from the bottom to the top electrode and is not influenced by the initial polarization direction.

Index Terms — **Nonlinear media, Ferroelectric films, Polymers, Dielectric polarization.**

1 INTRODUCTION

The investigation of dielectric nonlinearities is a powerful way to study the ferroelectric to paraelectric phase transition of ferroelectric materials. Compared to mere linear spectroscopy a variety of additional information can be obtained [1]. Nonlinear dielectric spectroscopy has been used to characterize the order of the phase transition, to determine the Landau parameters or to investigate the polarization and its temperature dependence in vinylidene fluoride-trifluoroethylene copolymers of various molar compositions. It is also applicable to record the temperature dependence of the remanent polarization and to detect non-switchable polarizations [2].

In recent years techniques for the preparation of thin VDF-TrFE copolymer films with thicknesses below 200 nm have been developed. These thin films are highly attractive for applications in e. g. nonvolatile memories [3] or pyroelectric sensors.

2 THEORY

2.1 DIELECTRIC NONLINEARITY

The dielectric response of a sample to an electric field shows nonlinearities which become more pronounced when the electric field strength is increased. In case of a nonrelaxational ferroelectric system in a monodomain state the nonlinearities can be described by a series expansion of the electric displacement D in powers of the electric field:

$$D = P_S + \varepsilon_0\varepsilon_1 E + \varepsilon_0\varepsilon_2 E^2 + \cdots \tag{1}$$

P_S is the spontaneous polarization and the ε_n's in equation (1) denote the nonlinear permittivities. For a sinusoidal excitation with electric field amplitude $E_\sim$ and circular frequency ω_0

$$E(t) = E_\sim \cos \omega_0 t \tag{2}$$

the response $D(t)$ of the sample contains components at harmonic frequencies:

$$D(t) = D_0 + D_1 \cos \omega_0 t + D_2 \cos 2\omega_0 t + \cdots. \tag{3}$$

The coefficients D_n can be determined by Fourier decomposition of the measured response $D(t)$ of the sample:

$$D_n = \frac{2}{T}\int_0^T D(t) \cos(n\omega_0 t)\, dt \tag{4}$$

In equation (4) $T = 2\pi/\omega_0$ is the signal period. Inserting equation (2) into equation (1) and comparing with equation

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