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

D. V. Nordheim, S. Hahne and B. Ploss*

Department of SciTec, University of Applied Sciences (FH) Jena, Carl-Zeiss-Promenade 2, 07743 Jena, Germany

Email: bernd.ploss@fh-jena.de

Abstract-**VDF-TrFE copolymer thin film of molar composition 70/30 and thickness below 70 nm has been prepared by spin coating on glass substrate covered with aluminum electrode. After polarization at room temperature by some hysteresis cycles, the linear and second order permittivities ε_1 and ε_2 have been studied over temperature in a heating and cooling cycle up to 120 °C i.e., above the Curie temperature. The temperature dependence of polarization is derived from ε_1 and ε_2. It is found that above 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.**

I. INTRODUCTION

The investigation of dielectric nonlinearities is a powerful tool to study the ferroelectric to paraelectric phase transition of ferroelectric materials. Compared to only 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 remanent polarization and to detect non-switchable polarization [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.

II. THEORY

The linear and second order permittivities ε_1 and ε_2 in the power series expansion of electric displacement D in powers of electric field E

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

can be measured by harmonic analysis of the current through a sample when a high purity sinusoidal voltage with amplitude far below the coercive voltage is applied. When the free energy F of the material is described by a Landau expansion

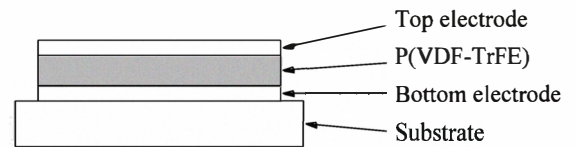$$F = F_0 + \frac{\alpha}{2} D^2 + \frac{\gamma}{4} D^4 + \frac{\delta}{6} D^6$$

Fig. 1. Sketch of the VDF-TrFE copolymer film deposited by spin coating on a glass substrate covered with an aluminum bottom electrode. The aluminum top electrode was deposited after annealing of the film.

the second order permittivity is expressed by [4]

$$\varepsilon_0 \varepsilon_2 = -P_r (\varepsilon_0 \varepsilon_1)^3 (3\gamma + 10\delta P_S^2)$$

When the term $3\gamma + 10\delta P_S^2$ does not change too strong with temperature, the expression $\varepsilon_0 \varepsilon_2 / (\varepsilon_0 \varepsilon_1)^3$ is essentially proportional to the remanent polarization P_r [5].

III. EXPERIMENTAL

VDF-TrFE copolymer with molar ratio 70/30 was dissolved in diethyl carbonate and film with 64 nm thickness has been deposited on glass substrate covered with an aluminum electrode by spin coating followed by annealing at 140 °C for 2 hours before a top electrode of aluminum was evaporated (see Fig. 1). The film was polarized by a few hysteresis cycles (Fig. 2) which were stopped at $E=0$ at $+P_r$. ε_1 and ε_2 were then measured at a frequency of 1 kHz in a heating and cooling cycle from 30 °C to 120 °C. The hysteresis poling was repeated at room temperature but now stopping at $-P_r$ and ε_1 and ε_2 were measured in a temperature cycle again.
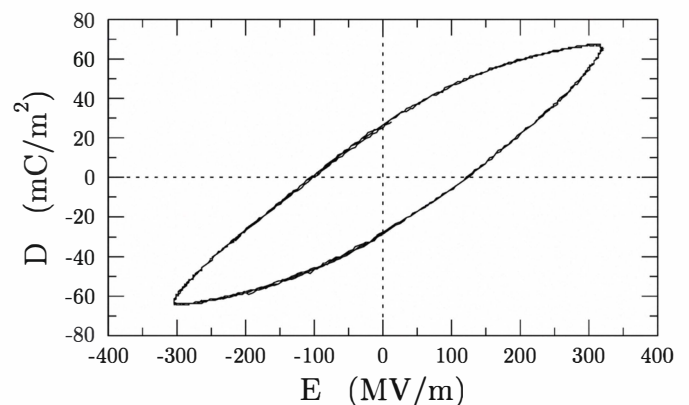

Fig. 2. Hysteresis loop of electric displacement D as a function of the electric field E measured on 64 nm thick 70/30 mol% VDF-TrFE copolymer film at 25 °C.