



Broadband dielectric dispersion in ferroelectric P(VDF-TrFE) copolymer films

Bjoern Martin*, Manfang Mai, Herbert Kliem

Institute of Electrical Engineering Physics, Saarland University, Campus A51, 66123 Saarbruecken, Germany

ARTICLE INFO

Article history:

Received 21 June 2012

Received in revised form

24 July 2012

Accepted 25 July 2012

Available online 2 August 2012

Keywords:

Broadband dielectric spectroscopy

Dielectric relaxation

Electrode effects

Ferroelectric polymers

ABSTRACT

Ferroelectric polyvinylidene fluoride-trifluoroethylene copolymer films with different thicknesses are prepared by a solvent-cast technique, by spin coating, and by a horizontal Langmuir–Blodgett technique respectively. The frequency dependent dielectric permittivity of these films is investigated with varying sample thickness and varying temperature in the ferroelectric as well as in the paraelectric phase. A dielectric relaxation according to a Vogel–Tamman–Fulcher law of the relaxation times is found in all samples. However, the relaxation times extracted from the dielectric permittivity in the frequency range are not consistent with the relaxation times determined from the temperature range. An explanation for this behavior is given by a temperature dependent distribution of relaxation times. Additionally, in thin samples a second relaxation with a weak anomalous temperature dependence, i.e. an increasing relaxation time with increasing temperature, is observed at high frequencies. Detailed investigations show that this behavior can be attributed to an electrode effect.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polyvinylidene fluoride (PVDF) and its related copolymers containing trifluoroethylene (TrFE) have been the focus of numerous investigations during the past years [1–23]. In our investigations they are prepared with different thicknesses and with different techniques. For example ultrathin films of P(VDF-TrFE) copolymer can be produced with a Langmuir–Blodgett (LB) deposition technique. It has been shown in former experiments that also these thin films with thicknesses down to 1 nm exhibit ferroelectric behavior [12]. Hysteresis curves of the polarization versus the applied electrical field with a remanent polarization of about $10 \mu\text{C}/\text{cm}^2$ are measured [13]. Furthermore, the polarization can be switched between two stable states with an external electrical field. Therefore, the P(VDF-TrFE) thin films are promising candidates for an application in electronic circuits as non-volatile ferroelectric random access memory devices [24–27].

Additionally, small signal broadband dielectric spectroscopy measurements show a pronounced dielectric relaxational behavior at frequencies of about 1 MHz at room temperature [11,15–21]. The temperature dependent behavior of the relaxation times is investigated with variation of the sample thickness and the preparation technique. The relaxation times extracted from the dielectric permittivity in the frequency range are not consistent with the relaxation times determined from the

temperature range. An explanation for this behavior is given in this paper.

Furthermore, a second dielectric relaxation with an anomalous shift of the relaxation times with the temperature is investigated in thin samples [16,17]. It is shown here why these relaxation times shift to longer times with increasing temperature.

2. Sample preparation and experimental setup

To fabricate a broad range of sample thicknesses three different preparation techniques are used, i.e. a solvent-cast technique for thicknesses ranging from $8 \mu\text{m}$ to $200 \mu\text{m}$, a spin coat technique for thicknesses between 50 nm and $2 \mu\text{m}$, and a horizontal Langmuir–Blodgett technique for ultrathin samples between 5 nm and 200 nm . For all preparation techniques a P(VDF-TrFE) (70:30) copolymer purchased from Piezotech S.A.S. (France) is used.

For the cast technique the P(VDF-TrFE) is dissolved in 2-butanone with concentrations of 3 or 5 wt%. The solution is cast in a form and dried in an oven at 403 K. Afterwards, the samples have the shape of a foil and can be removed from the form. Aluminum electrodes with an area of about 1 cm^2 are evaporated to the samples on both sides. Due to this sample geometry a simple measurement of the broadband dielectric relaxation spectra is possible.

For the spin technique the P(VDF-TrFE) is also dissolved in 2-butanone having lower concentrations between 1.5 and 3 wt%. A cleaned glass substrate is evaporated with aluminum stripes with a width of $200 \mu\text{m}$. The copolymer is spin coated onto the glass

* Corresponding author. Tel.: +49 681 302 4766; fax: +49 681 302 2272.
E-mail address: b.martin@mx.uni-saarland.de (B. Martin).

substrate and the sample is dried in an oven at 403 K. Aluminum electrodes perpendicular to the first ones are evaporated onto the film then. The crossing area of the aluminum stripes determines the active area.

The LB samples are prepared with P(VDF-TrFE) dissolved in dimethylsulfoxide with a concentration of 0.02 wt%. The films are transferred with the horizontal LB technique which allows the consecutive deposition of copolymer monolayers [7,13,23]. The electrode configuration and the drying process are identical with the configuration for the spin coated samples.

All samples used for the measurements were heated above the Curie temperature and cooled down again to room temperature. During the measurements no d.c. bias voltage is applied to the samples preventing a polarization of the samples due to an external field. However, a spontaneous polarization as typical for ferroelectrics can appear.

The measurements in the frequency range are performed with an Agilent 4294A impedance analyzer for frequencies between 40 Hz and 110 MHz and with an Agilent 4291A impedance analyzer from 1 MHz to 1.8 GHz. The measurements are carried out in dry atmosphere in shielded measurement cells which can be cooled down to 200 K and heated up to 400 K. The thicker cast samples are placed in a coaxial line adjusted to the characteristic impedance of the measurement system allowing measurements up to 500 MHz. Due to the different electrode configuration of the spin coated and of the LB films copper pads are evaporated onto the aluminum stripes. The inner conductors of coaxial lines are directly soldered to the copper pads. It should be noted that the use of contacting needles or silver paste yields measurement errors and unreproducible results under variation of the temperature.

For the temperature variation the measurement is started at room temperature and the sample is heated to about 393 K. Then, the sample is cooled down to about 213 K and heated up again to room temperature. During the heating and cooling cycles each 10 K a measurement of the complete frequency spectrum is performed to find the data in the frequency range with variation of the temperature, $\epsilon^*(f)$. In the same run the temperature and the dielectric permittivity at selected frequencies are measured each 30 s to get the data in the temperature range with variation of the frequency, $\epsilon^*(T)$.

3. Mathematical considerations

Measurements performed in the frequency range show a pronounced dielectric relaxation in P(VDF-TrFE) as described later. For a mathematical description of the data in the frequency range $\epsilon^*(f)$ the empirical Havriliak–Negami (H–N) formula:

$$\epsilon^*(f) = \epsilon'(f) - j \cdot \epsilon''(f) = \frac{\Delta\epsilon_{st}}{(1 + (j \cdot 2\pi f \cdot \tau)^\alpha)^\beta} + \epsilon_\infty \quad (1)$$

is often used as fit function [28,34]. Here, $\Delta\epsilon_{st}$ is the relaxational part of the static permittivity, ϵ_∞ the high frequency dielectric permittivity, and τ is the relaxation time. The parameter α describes a distribution of relaxation times ($0 < \alpha \leq 1$). The parameter β is connected to a shape of the distribution of relaxation times ($0 < \beta \leq 1$). In the case of a symmetrically shaped distribution β is equal to 1. For $\alpha = \beta = 1$ we find a Debye relaxation with only one single relaxation time.

A distribution of relaxation times can be caused by a distribution of activation energies W [32–34]. We assume now that the relaxation times follow a simple thermally activated Arrhenius behavior:

$$\tau = \tau_0 \cdot \exp\left(\frac{W}{k \cdot T}\right) \quad (2)$$

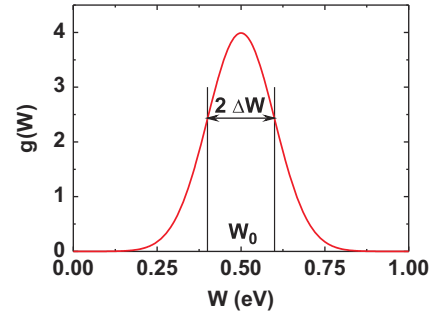


Fig. 1. Gaussian distribution function $g(W)$ according to Eq. (3) with $W_0 = 0.5$ eV, $\Delta W = 0.1$ eV, and $A \approx 4$.

with an activation energy W , the Boltzmann factor k , and the constant $\tau_0 = 10^{-12}$ s. The activation energies shall now be Gaussian distributed, i.e. the distribution function $g(W)$ is given as

$$g(W) = A \cdot \exp\left(-\frac{(W - W_0)^2}{2 \cdot \Delta W^2}\right) \quad (3)$$

using for example $W_0 = 0.5$ eV and $\Delta W = 0.1$ eV. With the normalization of $g(W)$,

$$\int_0^\infty g(W) dW = 1 \quad (4)$$

the prefactor $A = (dW \cdot \sqrt{k \cdot T})^{-1}$ can be determined. The Gauss function is plotted in Fig. 1. It should be stated that this temperature independent distribution of the activation energies yields a temperature dependent distribution of relaxation times [33]. The distribution of relaxation times is broadened for lower temperatures caused by the temperature dependent exponent in Eq. (2).

Now, the imaginary part of the dielectric permittivity ϵ'' can be calculated as

$$\epsilon''(f, T) = \Delta\epsilon_{st} \int_0^\infty \frac{(2\pi f) \cdot \tau_0 \cdot \exp\left(\frac{W}{k \cdot T}\right)}{1 + (2\pi f)^2 \cdot \tau_0^2 \cdot \exp\left(\frac{2W}{k \cdot T}\right)} g(W) dW \quad (5)$$

In Fig. 2(a) the imaginary part of the calculated dielectric permittivity $\epsilon''(f)$ in the frequency range with variation of the temperature is shown. It can be seen directly that the distribution of relaxation times is broadened for lower temperatures as expected. From the maxima of $\epsilon''(f)$ we find the main relaxation times of the process. It is assumed that $\Delta\epsilon_{st}$ is independent of temperature.

The H–N fit is used in Fig. 2(a). It can be seen that qualitatively the empirical H–N formula is consistent with a Gaussian distribution of activation energies over several decades around the main relaxation time [32–34]. Thus, the broadened dielectric relaxation spectra in the frequency range indicated by $\alpha < 1$ can be explained with a Gaussian distribution of activation energies. Furthermore, β is equal to 1 due to the symmetrical Gaussian distribution of activation energies. Here, the maxima of $\epsilon''(f)$ refer at each temperature to the maximum of the distribution of activation energies via Eq. (2) and $2\pi f \tau = 1$.

Additionally, the dielectric permittivity $\epsilon''(T)$ in the temperature range with variation of the frequency can be calculated from Eq. (1) as shown in Fig. 2(b). Here, relaxation times related to the maxima of ϵ'' versus the temperature can be identified.

The relaxation times extracted from the frequency range and from the temperature range are plotted in an Arrhenius representation as shown in Fig. 2(c). It can be seen that the curves do not coincide. This is due to the distribution of relaxation times which shifts the maximum of the imaginary part of the dielectric

Download English Version:

<https://daneshyari.com/en/article/1810570>

Download Persian Version:

<https://daneshyari.com/article/1810570>

[Daneshyari.com](https://daneshyari.com)