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Structure and ferroelectric properties of P(VDF-TrFE) films prepared under different conditions — Effect of filtration of the copolymer solution

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Vinylidene fluoride-trifluoroethylene copolymer films of molar ratio 70/30 with thickness of about 1 μm have been deposited from solution in ethyl methyl ketone to a glass substrate with an aluminum electrode by spin coating. The solution has been filtrated through a PTFE membrane filter with pore size 0.2 μm directly before spin coating or it has been used as is (unfiltrated). After deposition of a top electrode, the samples have been polarized by hysteresis loops with an electric field amplitude of about 100 V/μm. In samples, annealed at temperature 145°C for 3 h, a high remanent polarization of about 7.5 μC/cm^2 has been achieved, without significant differences between samples fabricated of filtrated or unfiltrated solution. Spherulitic lamella are growing in films fabricated of filtrated solution when they are heated above the melting temperature to 159°C for 3 min before the further annealing process at 145°C. These films show substantially lower remanent polarization below 4 μC/cm^2. Pyroelectric images recorded with a pyroelectric laser scanning microscope show that the spherulites have very small pyroelectric activity, i.e., the spherulites consist of flat-on lamella. In contrast, no spherulitic lamella are growing in films fabricated of unfiltrated solution heated above the melting temperature, melted and annealed under the same conditions. An explanation for this observation is that filtrating changes the structure of the copolymer in solution from polymer coil to rod. Copolymer rods deposited on a substrate will crystallize in flat-on lamella when heated above the melting temperature, in contrast to copolymer coils which crystallize in edge-on lamella.

Keywords: P(VDF-TrFE); ferroelectric; polymer; structure.

1. Introduction

The copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) is semicrystalline consisting of crystalline and noncrystalline regions. As ferroelectricity originates from the crystalline phase the degree of crystallinity is an essential factor for the performance of the material. To increase grain size and crystallinity, annealing processes are commonly applied to VDF-TrFE copolymer film deposited from solution. It is common to anneal the material at temperatures above the Curie temperature but below the melting temparature of the material.[1] Details in the annealing process are of high importance. Variations of the annealing temperature of 1 K only can have significant effect on the morphology and structure of VDF-TrFE copolymer films.

It is usually avoided to melt a film deposited from solution as the intensity of (110) + (200) diffraction peaks attributed to the β phase of P(VDF-TrFE) decreases.[2,3] Even irreversible extinction of ferroelectric polarization in spin-coated VDF-TrFE copolymer thin films upon melting and recrystallization has been observed.[4] It has been reported that the β-phase content shows its maximum at 140°C annealing temperature.[5] Morphologic transition from big grains to fiber-like rods has been observed for VDF-TrFE copolymer film of molar ratio 70/30 above the melting temperature.[6] However, not only decrease but also increase of the ferroelectric diffraction peak is reported in literature. For a spray-coated VDF-TrFE copolymer film it has been found that neither peak intensity nor degree of crystallinity decreases for annealing at 170°C.[7] It is also reported that annealing above the melting temperature results in an increase of the ferroelectric peak and the disappearance of peaks resulting from the nonpolar phase.[8]

Dust particles and other impurities in the polymer solution can generate defects in the deposited copolymer film which may e.g., cause a breakdown when the film is polarized under high electric field. A common procedure to remove such particles and increase the yield of high quality films is to filtrate the copolymer solution before deposition on a substrate. In our laboratory filtrated solution is sometimes used for the fabrication of copolymer film, but not always. Characterizing VDF-TrFE copolymer film prepared from unfiltrated and filtrated solution has led to the initially unexpected observation that filtering can have a significant effect on structure and ferroelectric properties. This was the motivation for a more detailed study presented in the following.

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