CONTROL OF $\beta$- AND $\gamma$-PHASE FORMATION IN ELECTROACTIVE P(VDF-HFP) FILMS BY SILVER NANO-PARTICLE DOPING

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Poly(vinylidene fluoride) (PVDF) and its copolymers has been widely studied due to their excellent multifunctional properties like ferro-, piezo- and pyro-electric and used in a wide range of applications, such as transducers, touch sensors, nano-generators, non-volatile memories and energy storage devices. PVDF trifluoroethylene copolymer (P(VDF/TrFE)) shows ferroelectric behaviour with high remnant polarization because of the fully electro-active polar $\beta$-phase namely the all-trans conformation ($TTTT$). In general, it is realized that the polarization of PVDF as well as of P(VDF/TrFE) can be influenced by the chemical modification of the material with chlorofluoroethylene (CFE), chlorotrifluoroethylene (CTFE) or hexafluoropropylene (HFP) groups. This leads for example to ferroelectric relaxor polymers with low remnant polarization [1] suggesting the use as high energy density materials.

Recently, a special attention onto P(VDF-HFP) copolymer has been paid regarding its application in the field of electric energy storage [2, 3]. It was found that mainly the electro-active crystalline phases, such as $\beta$- and $\gamma$- phases, play the vital role for any electronic and electrical application. For example, the $\beta$-phase with edge-on orientations (molecular chains parallel to the substrate) is suitable for non-volatile memory operation because of its easy dipole switching properties. In this orientation, the molecular dipoles ($\text{CF}_2$) are statistically distributed perpendicular to the substrate as the dipoles are perpendicular to the molecular chains. In contrast, a very high electric field is necessary to flip the dipoles in the face-on orientation (molecular chains perpendicular to the substrate). Therefore, the $\beta$-phase with edge-on orientations and the semi-electro-active $\gamma$- phase might be suitable for energy storage applications because of its stability under high electric fields and late polarization saturation [4]. However, to date, conventional uniaxial stretching technique was applied in order to induce the electro-active $\beta$- and $\gamma$- phases in P(VDF-HFP).

In this work, we demonstrate the generation of the electro-active $\beta$- and $\gamma$- phases in P(VDF-HFP) by in-situ silver nano-particle (Ag NP) doping and discuss the feasibility of associated applications. The prime advantage of this method is that electro-active films can be achieved in a wide thickness range of ultra-thin ($t \approx 80$ nm) to thick ($t \approx 30$ $\mu$m) without any further mechanical treatment. The Ag NPs incorporated films were prepared using Dimethylformamide (DMF) as reducing agent of AgNO$_3$ and P(VDF-HFP) as stabilizer. The edge-on orientations are clearly evident in our Ag NPs doped P(VDF-HFP) thin films prepared by spin coating. The ferroelectric response was checked by Dynamic Contact Electrical Force Microscopy [5]. Thick films were
produced by solvent casting. For these films we observed that the content of the β- and γ-phases inside the P(VDF-HFP) films can be tuned by the doping concentration (Fig. 1) as well as by the solvent casting temperature. The non-ionic state of silver is evident from the X-ray photo-electron spectroscopy (XPS) spectrum (inset of Fig. 1).

![Figure 1: FT-IR spectra of Ag NPs doped P(VDF-HFP) thick films (sample nomenclature: HF*Ag#, where * indicates the w/v concentrations of P(VDF-HFP) and DMF while # gives the AgNO₃ concentrations in mM). The top spectra is taken on the undoped P(VDF-HFP) thick film. The inset compares the Ag3d core level XPS spectra (excited with Mg Kα) of an undoped and a doped P(VDF-HFP) sample.](image1)

Furthermore, in-situ temperature dependent FT-IR was performed to determine the melting temperature of the crystalline polymorphs (α-, β-, and γ-phases). These data were cross-checked with Differential Scanning Calorimetric (DSC) results in order to avoid ambiguity and confusion of the melting points. Fig. 2 depicts the in-situ FT-IR spectra of a Ag NPs doped P(VDF-HFP) thick film, where the melting behaviour of the β- and γ-phases with respect to the temperature is clearly evident. The inset curves in Fig. 2 indicate that the peak melting temperature of the β-phase (mβp~125°C) is far below the peak melting temperature of the γ-phase (mγp~160°C) and the final melting of the β-phase (mβf) takes place when the peak melting of the γ-phase occurs. In addition, we have also found that the melting temperature of the α-phase is relatively higher than that of the β-phase but far below the γ-phase melting temperature.

![Figure 2: In-situ temperature dependent FT-IR spectra of a Ag NPs doped thick P(VDF-HFP) film (thermal ramp, 1°C/min.), where the spectra between 30°C and 140°C are shown in 10°C intervals and above 140°C in 5°C steps. The inset shows the absorbance intensities of the β-(1274 cm⁻¹ band) and γ-(1232 cm⁻¹) phases, where the peak and final melting temperatures are evident.](image2)