

Bandgap determination of P(VDF–TrFE) copolymer film by electron energy loss spectroscopy

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Abstract. The ferroelectric β of poly(vinylidene fluoride trifluoroethylene), P(VDF–TrFE) is confirmed for 100 nm thickness spin coated copolymer film. The homogeneous coverage of the copolymer film is investigated by the help of X-ray photoelectron spectroscopy (XPS). Most importantly, the existing bandgap in the crystalline phase of the copolymer is determined directly from the electron energy loss spectroscopy (EELS).

Keywords. Ferroelectric polymer; P(VDF–TrFE) film; β -phase; bandgap; EELS.

1. Introduction

Ferroelectric polymer polyvinylidene fluoride (PVDF) and its copolymer poly(vinylidene fluoride trifluoroethylene) (P(VDF–TrFE)) have generated tremendous attention due to their excellent properties for utility value. Over the last thirty years, P(VDF–TrFE) is the most studied ferroelectric polymer (Furukawa 1989). It has tremendous applications in electronic industry, such as soft transducers, infrared imaging, and compact capacitors and holds a promising future in the field of non-volatile memory (Auciello *et al* 1998; Henkel *et al* 2009). P(VDF–TrFE) crystallizes into various crystal forms depending on their molar content ratios of VDF (x) and TrFE ($1-x$), and on crystallization conditions (Lando and Doll 1968; Tashiro *et al* 1984a; Ohigashi 1985). Under ordinary pressure, the α crystal (most common polymorph) form consisting of alternating *trans-gauche* (TGTG) molecules packed in antiparallel fashion, is stable for the VDF homopolymer (PVDF), while the β phase crystal consisting of *all-trans* (TTTT) chains becomes more stable on introducing TrFE–(CHF–CF₂)–sequences into VDF–(CH₂–CF₂)–chains (Farmer *et al* 1972). The β phase crystal is well known to be of ferroelectric form, revealed by its D – E hysteresis loops (Furukawa *et al* 1980; Davis *et al* 1984), polarization switching (Tajitsu *et al* 1987), temperature behaviour of the dielectric constant (Furukawa *et al* 1980; Furukawa 1984; Tajitsu *et al* 1987) and anomalous X-ray dispersion (Takahashi *et al* 1987). The structural detail of the ferroelectric β phase is described by several workers (Lando and Doll 1969; Furukawa 1989;

Legrand 1989). Addition of the larger and less molar ratio of TrFE ruins the transition temperature by reducing the average dipole moment of the chains, expanding the lattice, and introducing defects. This ruined ferroelectricity on addition of TrFE reduces transition temperature (Lovinger *et al* 1984). In the present investigation, the composition of 70% VDF and 30% TrFE molar ratio is chosen, because it has the most distinct ferroelectric properties and can be made mostly crystalline without stretching treatments.

There are a few attempts to understand the electronic structure, band dispersions, band symmetries of PVDF and its copolymer (Tashiro *et al* 1984; Choi *et al* 1998; Duan *et al* 2003). However, until now there has been a lack of direct experimental evidence for bandgap estimation of the copolymer. We have employed an experimental technique, electron energy loss spectroscopy (EELS), to estimate the existing bandgap of the P(VDF–TrFE) copolymer, which is expected to have potential influence on material properties.

2. Experimental

The p type Si(100)-wafers (Wacker-Chemitronic GmbH) were used as main substrate for present investigations. Prior to preparation of polymer spin coated films, pieces of Si-wafers were cleaned through a standard RCA-1 cleaning procedure (Kern 1993). P(VDF–TrFE) (70 : 30) films with 9 μ m thickness were supplied by Piezotech S. A., France. 2.5% (w/w) copolymer solution was prepared with 2-butanone (AZ-EBR, microchemicals GmbH). Spin coating of copolymer on Si-wafer was performed inside glove box under Argon atmosphere. 4000 rpm spinning speed leads to 100 nm thickness of the copolymer film.

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After spin coating, the film was annealed at 135°C for 2 h to improve the crystallinity of the ferroelectric β -phase (Furukawa 1989).

Thickness of the spin coated film was determined by profilometer measurements (Taylor Hobbson, Tencor instruments). To confirm the β phase, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectra were taken. XRD was carried out in a 'XRD 3000 TT' device (Seifert-FPM Ahrendsburg, Germany) in Bragg Brentano geometry. The Co-K α radiation ($\lambda = 1.7902 \text{ \AA}$) is the source of the X-ray. FTIR spectra were recorded with Bio-Rad FTS-60A Spectrometer, equipped with deuterated triglycine sulfate (DTGS) detector and Thermo-Nicolet Impact 410 Spectrometers. Spectra were taken at 4 cm^{-1} resolution and 100 scans were recorded. Spectroscopic characterization by XPS was performed at room temperature in Omicron-UHV System with hemispherical analyzer (Hoffmann *et al* 2000). XPS survey scan was taken with Mg K α (1253.6 eV) excitation with a base pressure of 3×10^{-9} mbar. The electron energy loss spectroscopy (EELS) was carried out with Vacuum Workshop (VSW) Monochromator controlled electron range of 10–300 eV installed in Omicron UHV XPS system with a base pressure better than 1×10^{-9} mbar. In EELS experiment, two different analyser pass energies (2 eV and 5 eV) were used.

3. Results and discussion

3.1 Conformation of β -phase by showing results of XRD and FTIR

The FTIR spectrum is shown in figure 1. The analysis of FTIR spectra has been carried out for poly(tetrafluoroethylene) (Liang and Kirimm 1956; Hannon *et al* 1969; Masetti *et al* 1973) and for PVDF (Tashiro and Kobayashi 1989; Day *et al* 1992). These studies have proven to be enormously useful to select the vibrations in order to interpret the molecular structure of P(VDF-TrFE) copolymer. Due to the large mass of the fluorine atom, most infrared-active vibrations for the copolymer are concentrated in a rather narrow region, 1500–400 cm^{-1} (figure 1). Several vibrational bands for the copolymer have been assigned to specific conformations by Tashiro *et al* (1981, 1984b) and Tashiro and Kobayashi (1988, 1989) and these assignments are useful in the present analysis.

In figure 1, the bands marked with arrows, at 505 cm^{-1} , 845 cm^{-1} , 1184 cm^{-1} , 1290 cm^{-1} give evidence for *all-trans* ferroelectric phase. No indication for alternating *trans-gauche* conformation is observed. For this phase, a strong absorption feature at 802, 612 and 1196 cm^{-1} occurs, for example.

From the XRD measurement, it is clear that the P(VDF-TrFE) films show the crystalline region with

co-existence phase of amorphous region (see figure 2). It is well known that P(VDF-TrFE) has ferroelectric crystalline β -phase embedded in an amorphous matrix, and the β -phase has quasi-hexagonal close packing with orthorhombic *mm2* structure (Bune *et al* 1998). As shown in figure 2, the copolymer sample exhibits an intense diffraction peak at $2\theta = 23.4^\circ$, which is a characteristic diffraction peak of the ferroelectric polar β -phase of the overlapping (110) and (200) plane reflections (Davis *et al* 1978; Fernandez *et al* 1987; Bune *et al* 1998; Fang *et al* 2005).

3.2 XPS survey scan

The XPS survey scan (figure 3) clearly reveals that the absence of Si $2p$ core level around 99.3 eV binding energy, confirms the complete coverage of copolymer over the Si-wafer.

Furthermore, the spectrum consists of relatively narrow core-level (F1s and C1s) photoelectron peaks, a broad Auger transition peak and a valence band spectrum.

From the XPS spectra, the stoichiometric ratio (in atomic percent) of two elements, C and F, in the P(VDF-TrFE) film is determined. The relevant formula is as follows (Innes 1907):

$$\frac{n_C}{n_F} = \frac{I_C/S_C}{I_F/S_F},$$

where I_C and I_F are the peak area of C1s and F1s core level photoelectron peaks, respectively. S_C and S_F are the atomic sensitivity factors of carbon and fluorine, respectively. The calculated composition in atomic percent: C:F = 47.9:52.1, directly from XPS analysis, whereas

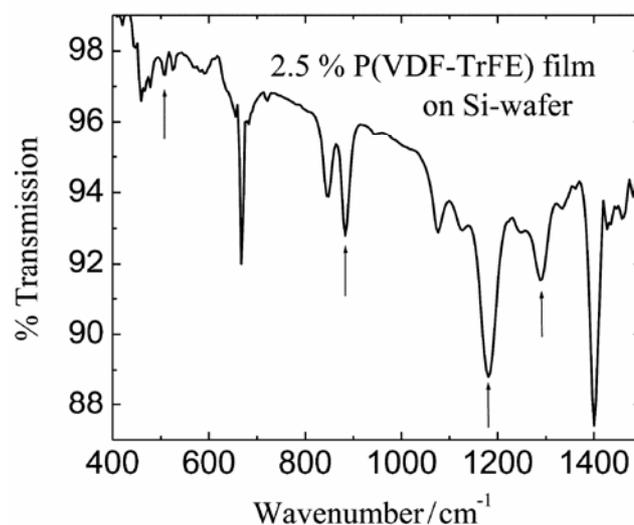


Figure 1. FTIR spectra of a 100 nm thick spin coated P(VDF-TrFE) film on a Si-wafer. The peaks, marked with arrows, correspond to *all-trans* ferroelectric phase.

according to a co-polymerization ratio of VDF:TrFE (70:30), the expected theoretical value for the ratio C:F = 46.5:53.5. Therefore, an XPS result shows excellent agreement with theoretical calculation.

3.3 EELS

By this method, a beam of mono-energetic, low-energy electrons, collimated on a surface, excite the lattice vibrations of the substrate, molecular vibrations of the absorbed species and even electrons. The energy loss of scattered electrons is described by the following equation:

$$E_{\text{EELS}} = E_0 - h\nu,$$

where E_{EELS} is the energy of the scattered electrons, E_0 the energy of the incident electrons, h the Planck constant and ν the frequency of the excited vibration.

One of the most advantageous features of EELS is that it can detect losses in a very broad energy range from infrared to electronic transitions at several electron volts.

A typical energy-loss spectrum shows a zero-loss i.e. elastic peak, constituting electrons that are un-scattered or scattered elastically in the specimen with negligible energy loss. Inelastic scattering is caused by electrostatic interaction between the incident and atomic electrons, and takes a variety of forms. In the case of semiconductor or insulator, excitation of valence electrons to the conduction band gives rise to a spectral component proportional to the joint density of states. The intensity, therefore, remains low up to an energy loss equal to the energy gap, essentially bandgap (E_g), allowing the latter to be measured. The surface or defect states are visible too.

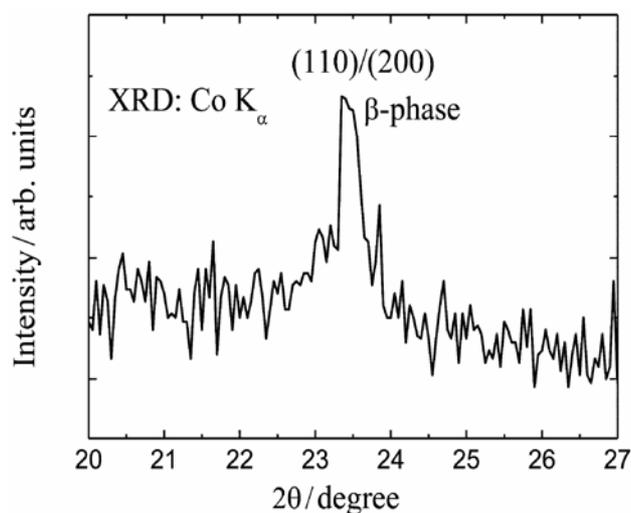


Figure 2. XRD pattern of 100 nm spin coated film of P(VDF-TrFE) on Si-wafer.

From FTIR and XRD investigations, it is confirmed that in 100 nm spin coated copolymer film have *all-trans* conformation of β -phase with amorphous surroundings. The theoretical calculations of band structure of PVDF polymer is one of the good points of the present study (Duan *et al* 2003). The principal of bandgap measurements by the EELS method is described by Kimoto *et al* (2005).

Figure 4 shows the EELS spectrum of the P(VDF-TrFE) copolymer film (thickness \sim 100 nm) obtained at an

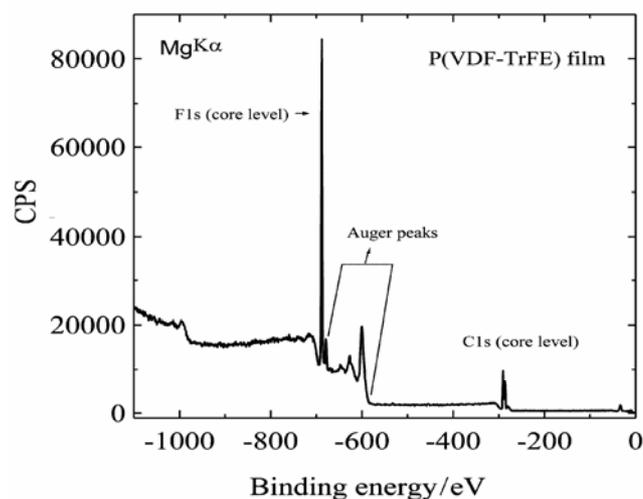


Figure 3. The XPS survey scan of 100 nm spin coated P(VDF-TrFE) copolymer film. The Mg K α ($h\nu = 1253.6$ eV) is used as an X-ray source.

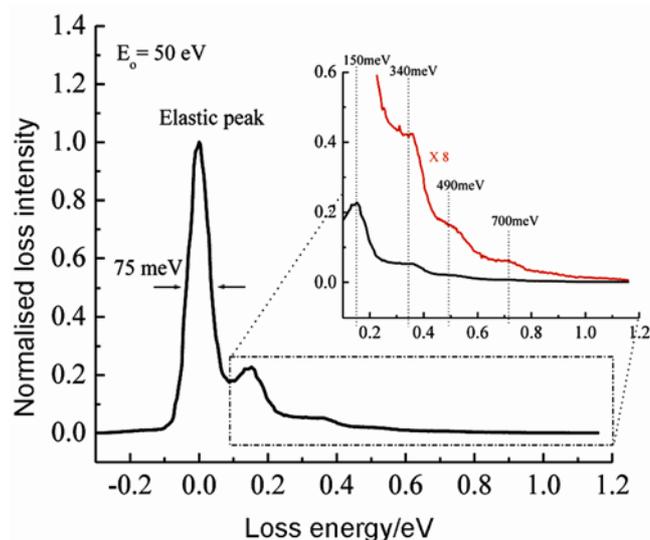


Figure 4. EELS spectrum of a 100 nm thick P(VDF-TrFE) copolymer film on Si(100), showing the most intense elastic peak, defect state and vibrational modes. E_0 denotes the primary electron beam energy and 75 meV ($= \Delta E$) as instrumental energy resolution. The inset presents the enlarged view of the vibrational modes.

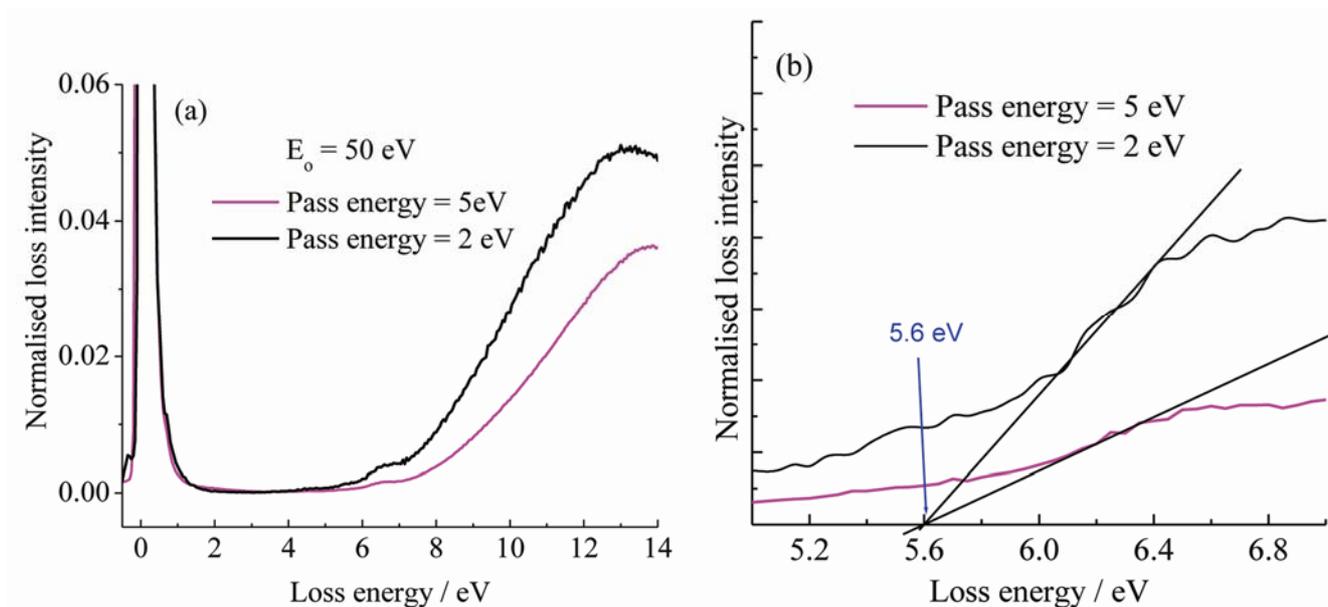


Figure 5. EELS spectrum of a 100 nm thick film of the P(VDF-TrFE) copolymer (a) measured for estimation of the bandgap and (b) enlarged view of the spectrum (a), showing the value of the bandgap (5.6 eV). E_0 denotes the primary electron beam energy.

incident primary electron beam energy (E_0) of 50 eV and with a instrumental energy resolution of 75 meV. The most intense peak indicates the typical elastic or zero loss peak arising in the EELS spectrum comprising electrons that are un-scattered or scattered elastically in the specimen with negligible energy loss ($E \sim 0$). The rest of the observable peak appears as shown in the inset of figure 4, the most intense peak arises due to existence of defects states and the rest of peaks show molecular vibrational modes (Shaw *et al* 1984).

Figure 5(a) shows the EELS spectrum of extended range of energy loss for bandgap determination for the sample. The bandgap value is estimated by the best linear fit of the loss intensity, extrapolated to loss energy as illustrated by figure 5(b). Therefore, the estimated bandgap (E_g) value is 5.6 eV. The measured E_g value in the present investigation is significant with the band structure model of PVDF crystal (Duan *et al* 2003).

4. Conclusions

The homogeneous P(VDF-TrFE) copolymer film with 100 nm thickness is prepared by spin coated method. The FTIR and XRD results support the semicrystalline behaviour of the film. The existence of the polar ferroelectric β phase is confirmed at room temperature for the present film. The evidence of *all-trans* ferroelectric phase and absence of alternating *trans gauche* conformation is clearly seen from the FTIR study. Furthermore, XRD results in a distinct diffraction peak which is characteristic of the β phase of the overlapping (110) and (200)

plane reflections. The calculated amount (in atomic percent) of the C and F present in the P(VDF-TrFE) film (C : F = 47.9 : 52.1) is close to the theoretical value (C : F = 46.5 : 53.5).

Finally, to understand the electronic properties of the copolymer film, EELS results are analysed. The conformation of the defects states and molecular vibrational modes are also conformed by EELS. Furthermore, the direct value of the bandgap (E_g) in the crystalline phase of the copolymer is determined. The investigated E_g value is 5.6 eV. Therefore, the present information in this paper should have realistic impact for the picture of band structure of the copolymer film.

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