



The effect of X-ray photoelectron spectroscopy measurement on P(VDF-TrFE) copolymer thin films

Dipankar Mandal^{a,b,*}, Klaus Müller^b, Karsten Henkel^b, Dieter Schmeißer^b

^a Department of Physics, Jadavpur University, Kolkata 700032, India

^b Brandenburgische Technische Universität Cottbus, Angewandte Physik-Sensorik, K.-Wachsmann-Allee 17, 03046 Cottbus, Germany

ARTICLE INFO

Article history:

Received 22 February 2012

Received in revised form 23 June 2012

Accepted 26 July 2012

Available online 3 August 2012

Keywords:

P(VDF-TrFE) copolymer thin film

XPS measurement

X-ray irradiation

Ferroelectric to paraelectric phase

transformation

ABSTRACT

The impact of prolonged X-ray irradiation during X-ray photoelectron spectroscopy (XPS) measurement was investigated on poly(vinylidene-trifluoroethylene) (P(VDF-TrFE)) thin films. It was observed that prolonged X-ray irradiation can accelerate the crosslinking of P(VDF-TrFE) and diminish the ferroelectric phase. Fourier transform infrared spectroscopy (FT-IR) data indicate that the ferroelectric phase diminishes completely after 360 kJ of X-ray irradiation dose and it induces the paraelectric phase. In this work, the main emphasis was given to the optimization of the X-ray irradiation dose during XPS measurements to maintain the ferroelectric phase within the copolymer films.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polyvinylidene fluoride (PVDF) and its copolymer Poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)), are well known due to their excellent ferro-, piezo-, and pyro-electric properties. These polymers are used in a wide range of applications, such as transducers in ultrasonic medical imaging [1], blood pressure and pulse measurements [2], touch sensors in robotics [3], non volatile memories [4–6], and nano-generator as energy harvesting devices [7].

PVDF (formula: $-\text{[(CH}_2\text{-CF}_2\text{)]}_n\text{-}$) has diverse crystalline phases (α , β , γ and δ) depending on the crystallization conditions [8]. The most common and non polar polymorph is the α -phase, it consists of alternating *trans-gauche* (TGTG) molecules packed in an antiparallel fashion. The β -phase has an *all-trans* (TTTT) planner zigzag structure and the dipole moments of the C–F and C–H bonds add up to an effective dipole moment in the direction perpendicular to the carbon backbone. Therefore, the β -phase has the largest spontaneous polarization per unit cell and thus exhibits the most superior ferroelectric and piezoelectric properties. An intermediate conformation is T_3GT_3G which favors a parallel packing

to generate the γ -phase. The parallel version of the α -phase is known as the δ -phase. The γ - and δ -phases are polar but their dipole moment is significantly smaller [9]. Therefore, the β -phase of PVDF is of a prime interest for electronic applications. In order to induce the β -phase in PVDF, primarily a special stretching treatment is required [8]. This is one of the major obstacles to use PVDF in organic electronics where the preparation of ultra thin films is one of the major requirements, i.e. a mechanical treatment is not applicable [10]. It was found that the P(VDF-TrFE) copolymer (formula: $-\text{[(CH}_2\text{-CF}_2\text{)-(CFH-CF}_2\text{)]}_n\text{-}$) crystallizes directly into the β -phase when a VDF content of 50–80% is used [8]. Therefore, the technological relevance of P(VDF-TrFE) has increased. X-ray photoelectron spectroscopy (XPS) analysis has been realized to be the most important tool for the investigation of the surface and interface properties of thin P(VDF-TrFE) films [7,11–15]. For example, recently we have demonstrated by XPS analysis the presence of a non ferroelectric layer AlF_2 in the case of aluminum electrodes on P(VDF-TrFE) [12]. As a consequence, these films show lower remnant polarization than films with organic electrodes prepared from poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) [16].

To date, there has been no specific report on P(VDF-TrFE) thin films about the impact of X-ray irradiation during XPS measurement itself, especially for prolonged measurement duration. There has been only a similar type of attempt on pure PVDF reported in Ref. [17]. Therefore, the main issue of this work is to discuss whether the ferroelectric β -phase of thin P(VDF-TrFE) films can be retained during X-ray irradiation in XPS measurements.

* Corresponding author at: Jadavpur University, Department of Physics, 188 Raja S.C. Mallik Road, Kolkata 700032, India. Tel.: +91 33 2414 6666x2880; fax: +91 33 2413 8917.

E-mail address: dipankar@phys.jdvu.ac.in (D. Mandal).

2. Experimental

2.1. Thin film preparation

The P(VDF-TrFF) (70:30 mol%) copolymer was obtained from Piezotech S.A., France, in the form of 9 μm thick film sheets. The 2.5 wt% (w/v) copolymer solution was prepared by dissolving the copolymer sheet in 2-butanone. The thin film was prepared by spin coating technique in an inert glove box atmosphere. In this study, the film of 100 nm thickness was spin coated on a p-type Si(100)-wafer with a spinning speed of 4000 rpm. The film thickness was measured by a Taylor Hobson profilometer (Talystep). Prior to spin coating, the Si-wafer was cleaned by a standard cleaning method (RCA-1) in order to remove organic and undesired particles from the surface [18]. After spin coating, annealing was carried out in ambient environment at 135 °C for 2.0 h to remove residual solvent as well as to improve the degree of crystallinity [8].

2.2. Measurement techniques

The XPS spectra were recorded using an Omicron-UHV-System with hemispherical electron analyzer (EA 125) [19]. The X-ray photons were delivered from a commercial Mg K α source (1253.5 eV). The base pressure was $\sim 10^{-9}$ mbar. The X-ray source was operated at a high voltage of 10 kV with a filament emission current of 10 mA. The stray electrons were suppressed by a thin aluminum film placed in front of the X-ray source and the surface charging effect was compensated by using a flood gun. A pass energy of 20 eV was used for high-resolution (C1s, F1s) spectra. In this study, one set of XPS measurements (i.e. survey scan with 1.0 eV steps and a scan number of 4 and the high resolution C1s and F1s core levels with 0.1 eV steps and a scan number of 10 numbers) were recorded within 15 min. The X-ray irradiation dose was calculated by the product of the wattage of the X-ray anode (X-ray filament emission current \times the potential difference between it and the X-ray anode) and the irradiation duration. Therefore, an 90, 360, 720, 2160 kJ X-ray irradiation dose correspond to 0.25, 1, 2 and 6 h X-ray irradiation. The C1s and F1s XPS spectra were normalized and binding energy corrected with respect to the $-\text{CH}_2-$ and F1s main lines, respectively. The consciousness about the measurement duration is one of the important factors, especially for fluoro polymer based materials. Therefore, after XPS measurements, the structural changes (if any) were checked by Fourier transform infrared spectroscopy (FT-IR) measurement and compared with pristine films. The FT-IR spectra were taken in transmission mode by a FTS 60B Bio Rad spectrometer, equipped with deuterated triglycine sulfate (DTGS) detector. In each measurement, 100 scans with 4 cm^{-1} resolution were used. After 6 h of X-ray irradiation (dose: 2160 kJ) in the XPS chamber, near edge X-ray absorption spectroscopy (NEXAFS) was performed at the UG49/2 PGM 2 beam line (BESSY-II, Berlin, Germany) in the total electron yield mode. The details of the NEXAFS measurements, spectral normalization, background correction and curve deconvolution procedure have been described elsewhere [20].

3. Results and discussion

3.1. XPS analysis

Fig. 1 shows high resolution C1s XPS spectra of X-ray irradiated P(VDF-TrFE) film (thickness ~ 100 nm). Since the peaks have partially overlapping components, the curve has been deconvoluted into best-fitting Gaussian-Lorentzian components which are depicted in the figure. The fact that the C1s photoelectron peak from each type of carbon is distinctly different in binding energy, makes XPS an excellent tool to investigate these

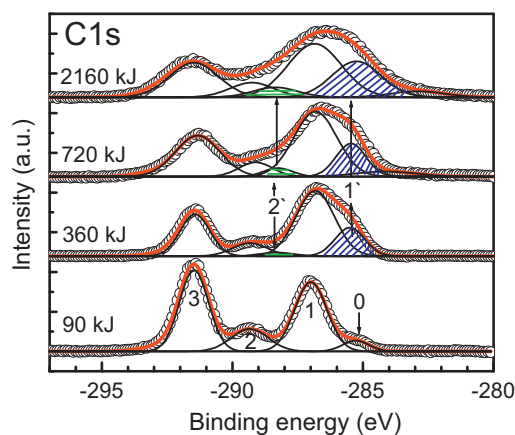


Fig. 1. High resolution C1s XPS spectra of the X-ray irradiated P(VDF-TrFE) films. The X-ray doses are labeled at the corresponding spectra. The assignment of the 0, 1, 2, 3, 1', 2' peaks are labeled in Table 1.

Table 1

Assignment of the C1s components^a of the pristine and X-ray irradiated P(VDF-TrFE) films.

Peaks	Binding energy(eV)	C1s species
0	285.3	Hydrocarbon contaminants
1	287.0	$-\text{CH}_2-$
2	289.3	$-\text{CFH}-$
3	291.5	$-\text{CF}_2-$
1'	285.5	$>\text{CH}-$
2'	288.4	$>\text{CF}-$

^a These results are evaluated from the C1s core level spectra, shown in Fig. 1.

materials [11,13,14,17,21,22]. As shown in Fig. 1, three major well-separated components and a small tail are illustrated in the pristine film. The highest binding energy component (291.5 eV) is from the $-\text{CF}_2-$ species, whereas the major lowest binding energy peak (287.0 eV) corresponds to $-\text{CH}_2-$ species [11,13,22]. In between these two major components, a well resolved small component at 289.3 eV can be observed, which arises due to the $-\text{CFH}-$ species [22]. The low energy tail at 285.5 eV might be attributed to hydrocarbon contamination [22]. The ratio of the peak areas of the $-\text{CF}_2-$, $-\text{CFH}-$ and $-\text{CH}_2-$ components of the 90 kJ irradiated film (8.5:3.0:8.0) is quite consistent with the theoretical value of 10:3:7. Due to the prolonged X-ray irradiation (i.e. dose 360 kJ or so), the asymmetry of the $-\text{CH}_2-$ peak became prominent and the contribution of two additional peaks (labeled as 1' and 2' in Fig. 1) is realized, it is depicted from the curve fitting of the high resolution C1s spectra. The detailed evaluation of the C1s peak identification is given in Table 1. The variations of the three prime carbon components ($-\text{CF}_2-$, $-\text{CFH}-$, $-\text{CH}_2-$) of P(VDF-TrFE) are plotted as a function of the X-ray irradiation dose, shown in Fig. 2a. The peak area of the $-\text{CH}_2-$ species is increased with irradiation dose whereas the $-\text{CF}_2-$ and $-\text{CFH}-$ contributions behave different. The additional two peaks in the spectra of the prolonged irradiated samples are corresponding to $>\text{CH}-$ (peak 1') and $>\text{CF}-$ (peak 2') species. These two carbon components are also increasing with the irradiation dose, as depicted in Fig. 2b. The entire phenomena can be explained by the reaction phenomena, illustrated in Scheme 1. These reaction scheme is described by a two step process, the first one is de-fluorination (three different possibilities of fluorine loss) and in a second step a crosslinking between the de-fluorinated chains occurs, as a result the $>\text{CH}-$ and $>\text{CF}-$ components are increased as observed in the C1s spectra (Figs. 1 and 2b). As described above, after one hour X-ray irradiation (dose: 360 kJ) a rapid fluorine loss was observed, thereafter the fluorine content became almost steady (Fig. 2a). The fluorine loss can be attributed

Download English Version:

<https://daneshyari.com/en/article/5364528>

Download Persian Version:

<https://daneshyari.com/article/5364528>

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