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Subgap absorption in poly(*p*-phenylene vinylene)

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Abstract

The subgap absorption of sulfonium chlorine precursor route PPV films has been studied by photothermal deflection spectroscopy. Two distinct features have been observed — a shoulder in the exponential region at 2.3 eV and a subgap absorption band centred at 1.6 eV. The latter is superimposed on an absorption smoothly decreasing to lower energy which magnitude correlates with the photoluminescence quantum efficiency. Similar features have been observed also for sulfonium precursor route dimetoxy substituted PPV and for soluble dialkoxy PPV.

Keywords: Poly(*p*-phenylene vinylene); Photothermal deflection spectroscopy; Photoluminescence quantum efficiency; Subgap absorption

1. Introduction

The conjugated polymer poly(*p*-phenylene vinylene), PPV, finds application in various optoelectronic devices [1] which stimulates the investigations of the energy states below the absorption edge. These states can act as traps and non-radiative recombination centres and the knowledge of their presence and nature gives important information for the improvement of the optoelectronic device performance. One experimental method for their investigation is the optical absorption. Photothermal deflection spectroscopy (PDS) is most suitable for that purpose and several authors [2–5] have applied it to PPV films. A steep exponential region has been observed below the absorption edge followed by a subgap absorption decreasing smoothly to lower energies. The absolute value of the latter varies between different publications [2–5]. In some spectra [2,4], the multiphonon absorption can be seen.

In the present paper, we present the main results of our PDS investigations of PPV films and correlate these results with the data for the photoluminescence quantum efficiency (PLQE).

2. Experimental

The samples were prepared as cast films on quartz substrates via the sulfonium chlorine precursor route [6] and thermally converted in nitrogen atmosphere for 1 h. The thickness of the films was about 3 μm. An experimental PDS setup was realised which allowed to get more insight into the low absorption region of the PPV films compared to our previous studies [5]. The standard optical scheme [7] was extended with a pyroelectric detector placed behind the sample for measurement of the transmitted light so that the measurement range of the system is $10^{-4} < \alpha d < 3$. The extended measurement range as well as the suppression of the interference fringes in the ratio of the absorbed to the transmitted light are the principal advantages of this measurement scheme [8,9].

The photoluminescence quantum efficiency (PLQE) was measured by an integrating sphere and a spectrograph coupled with a CCD detector. The excitation was at 442 nm from an GaN-LED with an interference filter. One and the same sample was used for the PDS and the PLQE measurements. The measurement procedure and the data analysis were performed using the optical scheme and the notations of de Mello et al. [10]. The simultaneous measurement in the spectral range of the excitation light and of the photoluminescence can be made in three configurations. Configuration a — sample outside the sphere, configuration b — sample in the sphere, not directly illuminated by the excitation beam, configuration c — sample illuminated by the excitation beam. The following equations describe the number of photons in the spectral range of the excitation L and of the photoluminescence P in configurations a, b, and c, where η is the PLQE, μ the coefficient describing the part of the excitation light scattered by the sphere and absorbed by the sample, A is the absorption of the

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sample at the excitation wavelength under direct illumination

$$L_{\mathrm{b}} = (1 - \mu)L_{\mathrm{a}} \tag{1}$$

$$P_{\mathrm{b}} = \eta\mu L_{\mathrm{a}} \tag{2}$$

$$L_{\mathrm{c}} = (1 - \mu)(1 - A)L_{\mathrm{a}} \tag{3}$$

$$P_{\mathrm{c}} = \eta[1 - (1 - \mu)(1 - A)]L_{\mathrm{a}} \tag{4}$$

There are three different solutions for η corresponding to measurements in configurations a and b Eqs. (1) and (2), a and c Eqs. (3) and (4), and b and c Eqs. (1)–(4). Therefore, the evaluation of the PLQE can be made by measurements in only two configurations. The results in the present paper were obtained by measurements in configurations b and c using Eq. (5).

$$\eta = \frac{P_{\mathrm{c}} - P_{\mathrm{b}}}{L_{\mathrm{b}} - L_{\mathrm{c}}} \tag{5}$$

The equation for evaluation of the PLQE proposed in [10] can be obtained from Eqs. (2) and (4), and represents a partial solution of this system of equations

3. Results and discussion

Using the above described PDS setup, we measured a large set of samples and observed the presence of a well defined band at about 1.6 eV and a shoulder at about 2.3 eV (Fig. 1). Since, the properties of the films are strongly dependent on the conversion conditions [6] we studied the subgap absorption for films prepared at different conversion temperatures. It is known [6] that the increase of the conversion temperature results in red shift of the absorption edge. The same trend is seen also for the exponential slope of the spectra in Fig. 1. The presence of such an exponential part in the spectrum of the absorption coefficient is characteristic for amorphous as well as for monocrystalline samples [11]. It is caused by the existence of internal potential fluctuations of different origin, whereas the slope is a measure of the magnitude of these fluctuations. The exponential slope is schematically shown as dashed lines in Fig. 1. The shoulder in this spectral range at 2.3 eV grows in intensity with the conversion temperature and reaches values comparable to those detectable by transmission measurements whereas its energy position remains constant. The exponential slope is nearly the same at energies higher and lower than this shoulder which was seen in the spectra for films thinner than 1000 nm (not shown). We detected a similar feature also for the soluble dialkoxy PPV. All these observations imply that a definite structural configuration typical for the conjugated polymer PPV can be the microscopic reason. Because of the high intensity of this feature of more than 10^3 cm^{-1} for the conjugated PPV it can not be ascribed to defect states.

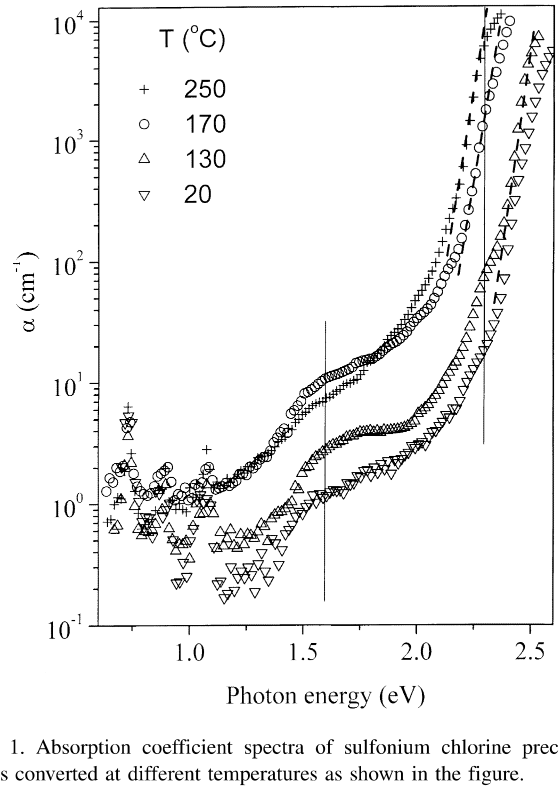

Fig. 1. Absorption coefficient spectra of sulfonium chlorine precursor films converted at different temperatures as shown in the figure.

Below the exponential part of the absorption spectrum a region of a smooth subgap absorption starts which is superimposed by a band centred at 1.6 eV. The smooth subgap absorption increases with the conversion temperature with the main changes taking place in the temperature range 130–170°C similar to the red shift of the exponential slope and the results of the transmission measurements [6]. The smooth background absorption extends to energies below 1.3 eV where the multiphonon absorption takes place [2].

The PLQE reflects also the crucial changes in the optical properties of the films for conversion temperatures in the range 130–170°C. Fig. 2 shows a decrease by more than a factor of two of the PLQE. The changes in the PLQE correlate well with the development of the smooth subgap absorption at energies below 2.1 eV. The integrated intensity of the absorption in the spectral range 2.15–1.2 eV after subtraction of the exponential slope shows the opposite behaviour compared with the PLQE (Fig. 2). Hence, the defect states leading to the subgap absorption promote the reduction of the PLQE being, however, not the only reason. The storage on ambient air, for example, did not influence significantly the subgap absorption whereas the PLQE was strongly reduced.

The band centred at 1.6 eV has different behaviour with the conversion temperature. If the smooth subgap absorption below this band is subtracted it can be seen that its intensity does not change significantly for conversion temperatures in the range 130–170°C. The intensity of the band at 1.6 eV develops at relatively low temperatures below 100°C and is very low in the film converted at 250°C. It has to be mentioned that the conversion process starts even at room

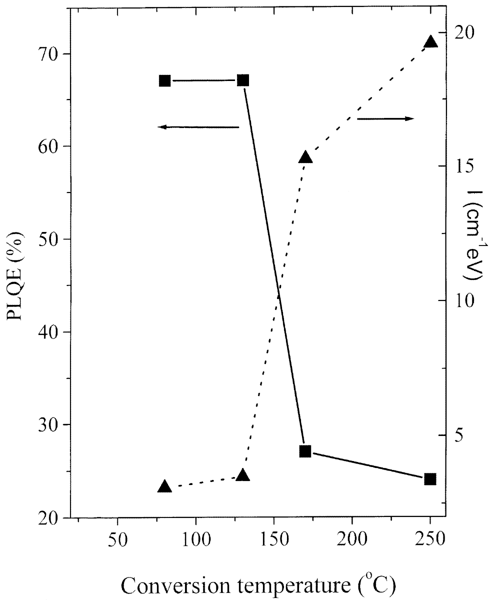

Fig. 2. PLQE (squares) and integrated intensity of the subgap absorption in the spectral range 2.15–1.2 eV (up triangles) vs. the conversion temperature.

temperature which is seen in the different optical properties of the cast films immediately after the deposition and several hours after that (not shown). Since, the lowest spectrum in Fig. 1 is for a film studied several hours after casting it can be considered as a film converted at room temperature and not as an "as deposited" film. The behaviour of the band at 1.6 eV with the conversion temperature implies that it is related with intermediate structural configurations appearing in the first step of the elimination of the leaving groups [6]. These structural configurations are removed at higher elimination temperatures. The corresponding energy states may act as deep trap states for the charge carriers because of their position deep within the energy gap. A similar well developed band with a peak value of 100 cm^{-1} at 1.38 eV was detected also for dimethoxy substituted PPV films. The higher intensity is probably due to the chemistry of the dimethoxy substituted polymer promoting the preferential formation of the specific structural configurations leading to this subgap absorption band.

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