Electric-field-induced optical second-harmonic generation in poly(phenylene vinylene) light-emitting diodes

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Abstract

We demonstrate second-harmonic generation in polymeric light-emitting diodes built in a layer structure of indium tin oxide, poly(phenylene vinylene) and aluminum. The second-harmonic intensity generated in the active zone of the diode depends quadratically on the applied reverse bias. In order to account for the bias dependence of the measured intensity a simple model is given in that the signal consists of two contributions: a constant, bias-independent contribution from the indium tin oxide/poly(phenylene vinylene) interface and a second one that depends on the effective bias at the organic metal±semiconductor contact. Further applications for second-harmonic generation in organic semiconductors are discussed.

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1. Introduction

Due to its high intrinsic surface sensitivity second-harmonic generation (SHG) has been established as a very powerful tool for the analysis of surfaces and interfaces. Especially in the field of metal oxide semiconductor interfaces various investigations have been performed recently [1–3]. Within this framework the influences of external static or high-frequency electric fields on the SH intensity were extensively investigated. These electric-field-induced second-harmonic (EFISH) measurements allow an in situ determination of important quantities in electrical devices or high-frequency circuits with very high time resolution up to the GHz domain. The purpose of this paper is to demonstrate that the EFISH technique [4,5] can also be applied to organic semiconductor devices like poly(phenylene vinylene) (PPV); a commonly used material for the fabrication of organic light-emitting diodes, LEDs.

Diodes based on PPV have been extensively studied due to possible applications in display technology [6]. We consider EFISH in particular being interesting for PPV diodes since SHG in PPV is forbidden by symmetry. In contrast to thermal poling experiments the EFISH technique allows an in situ investigation at normal operating temperature and leads to nonpermanent nonlinear susceptibility [7,8].
2. Experimental

The LEDs used for our experiments are built up in a layer structure as shown in Fig. 1, consisting of a glass substrate, a 100 nm indium tin oxide (ITO) layer as transparent electrode, a 300 nm poly(phenylene vinylene) layer and an aluminum (Al) top electrode; details of the fabrication processes are published elsewhere [9]. Since the ITO and the aluminum layer are structured in a stripe pattern perpendicular to each other, the active zone of the diode (ITO/PPV/Al) is the resulting square of 5 mm × 5 mm where the two stripes overlap. The samples thus have various regions where the individual interfaces can be investigated by SHG separately. For the measurements the sample was attached with its glass side onto a prism using glycerin as immersion. All measurements were performed under normal incidence on the cathetus of the prism. The laser setup consisted of a Nd:YAG laser (8 ns, 10 mJ, 1064 nm, 10 Hz) and a standard monochromator/photomultiplier combination for the SH detection (for details, cf. Ref. [10]). A polarizer and an analyzer allow polarization-dependent excitation and detection. In order to prevent light-induced damage to the diode the pulse energy of the fundamental was kept below 5 mJ at a beam diameter of ~1 mm. To perform bias-dependent measurements in the active zone of the diode, the electrodes of the sample were connected to a computer-controlled power supply. In order to prevent degradation of the diode, measurements were performed with a maximum reverse bias of 20 V and a forward bias not exceeding 2 V.

Second-harmonic measurements at different positions on the sample allow to separate the contributions of the various interfaces to the SH signal. For these measurements both excitation and detection were performed in p-polarization without applying any bias to the diode. PPV on glass shows no significant SH intensity corresponding to the expectations for a centrosymmetric material, whereas in the ITO/PPV, the PPV/Al and the ITO/PPV/Al region a signal is observed. The measured signal was verified as a SH signal by its spectral properties and its intensity dependence. The signal in the active zone of the diode is shown in Fig. 2. Even if no bias is applied, a SH signal is detected. With increasing reverse bias, the SH intensity first decreases to a minimum value before increasing quadratically. For a maximum reverse voltage of 20 V (ITO biased negatively), the SH intensity is 25 times larger than that of the unbiased diode.

3. Explanation of the bias dependence

In order to account for the observed bias dependence we present the following phenomenological model. At first, we give an explanation for the fact that there is a bias-dependent signal at all. The physical properties of the PPV/Al contact can be well described by the model of a Schottky contact [11,12]. At the contact, there is a depletion region exhibiting a bias-dependent width $d$. This width is proportional to the square root of the effective bias $U_{\text{eff}}$

$$d \propto \sqrt{U_{\text{eff}}} \propto \sqrt{U_D - U} ,$$

where $U_D$ is the applied bias, $U_{\text{eff}}$ is the effective bias, and $U$ is the applied voltage. The measured signal was fitted to the data based on Eq. (4) with $U_{\text{eff}} = 1.8$ V, $\Delta \varphi = 139.3(21)^\circ$, $\chi^{(2)} = 4.35(14)$ a.u. and $\chi^{(2)} = 0.769(14)$ a.u. for the centrosymmetric material, whereas in the ITO/PPV, the PPV/Al and the ITO/PPV/Al region a signal is observed.
where $U$ denotes the external applied bias and $U_D \approx 1.5$ V is the diffusion voltage which is defined as the potential difference over the Schottky contact in the unbiased case.

In the depletion region, a polarization is induced in PPV by the electric field $E_0(z)$, hence the centrosymmetric symmetry is broken and a signal can be detected. The electric-field-induced second-harmonic generation can be described by the third-order susceptibility $\chi^{(3)} = \chi^{(3)} (-2 \omega; \omega, \omega, 0)$. In the following we assume that phase matching can be neglected. This is justified because the thickness of the depletion region ($\sim 100$–200 nm) is one order below the coherence length of the second-harmonic process. With this assumption, the SH intensity $I_{2\omega}$ for $U \leq U_D$ is given by

$$I_{2\omega} \propto \left| \int_0^d \chi^{(3)}(-2 \omega; \omega, \omega, 0) E_0^2 E_0(z) \, dz \right|^2,$$

$$\propto \left| \chi^{(3)} I_{2\omega} \int_0^d E_0(z) \, dz \right|^2,$$

$$\propto \left| \chi^{(3)} (U_D - U) \right|^2 I_{2\omega}^2.$$

This gives the remarkable result that the SH intensity does not depend on the width $d$ of the depletion region under this approximation. On first sight this seems to be contra-intuitive, but if we keep $U$ constant the dc electric field $E_0$ is decreasing with increasing width $d$. Since the SH intensity is roughly proportional to $(\chi^{(3)} E_0 d)^2$ both effects compensate each other.

With Eq. (4) we expect a branch of a parabola shifted to the right by the diffusion voltage $U_D$. However, Fig. 2 shows a minimum shifted to the left. This deviation can be explained by a constant, bias-independent contribution $\chi_{\text{const}}^{(2)}$ to the SH signal from other interfaces. As illustrated in Fig. 3, the total signal is determined by the complex addition of these two contributions. With $\chi_{\text{eff}}^{(2)}(U) = \chi^{(3)}(U_D - U)$ and $\Delta \phi$ being the phase difference of the two contributions, the SH intensity can be calculated as

$$I_{2\omega} \propto |\chi_{\text{eff}}^{(2)}(U)|^2 + |\chi_{\text{const}}^{(2)}|^2 I_{2\omega}^2,$$

$$\propto \left( |\chi^{(3)}|^2 (U_D - U)^2 + |\chi_{\text{const}}^{(2)}|^2 + 2 |\chi_{\text{const}}^{(2)}| |\chi^{(3)}| \times (U_D - U) \cos \Delta \phi \right) I_{\omega}^2.$$

Using this equation, the experimental data can be fitted quite well with $\Delta \varphi = 139.3(21)^\circ$. $\chi_{\text{const}}^{(2)}$ = 4.35(14) a.u. and $\chi^{(3)}$ = 0.769(14) a.u. as shown by the solid line in Fig. 2, where $U_D = 1.8$ V was assumed. Since we do not measure absolute intensities, only the relation $\chi_{\text{const}}^{(2)} / \chi^{(3)} = 5.66$ V can be obtained in absolute units. We assume that the constant contribution mainly results from the ITO/PPV interface as was verified by a reference measurement in the ITO/PPV region giving a signal of appropriate magnitude. The SH activity of the ITO/PPV interface is well known in the literature [14].

4. Time-resolved measurements

Fig. 4 shows the build-up of the SH signal on a microsecond time-scale after switching on a reverse bias of $U_0 = 21.5$ V. In this experiment, a sampling technique is used where the time delay between the rising edge of the bias and the laser pulse was varied as depicted in the inset of Fig. 4. The measured time dependence reflects the charging process of the diode which has a high capacitance due to the large area of the device and the small distance between the electrodes. The SH signal depends quadratically on $U(t) = U_0(1 - \exp(-t/\tau))$ according to Eq. (6). The time constant $\tau$ is given by the product of this capacitance $C$ and the internal resistance $R$ of the driving circuit, i.e. $\tau = RC$. With this simple model the observed time dependence can be fitted quite well with $\tau = 1.12$ μs, as shown by the solid line in Fig. 4. In addition, the experimental data prove that
the bias dependence is reproducible and only due to reversible electric-field-induced processes. In contrast to thermal poling experiments [7] no permanent effects remain after the bias is switched off.

Time-resolved measurements of this kind may be helpful in future experiments to investigate space charge effects like charge injection and trapping that influence the device.

We also investigated the bias dependence of the second-harmonic in forward direction. Since our setup had no encapsulation to protect the diode from degradation under forward bias, the response of the diode changed dramatically during operation. For that reason we were not able to find out a reproducible correlation of bias, current and SH intensity. However, after degeneration the diode does not allow high current in forward direction due to the build-up of a high-resistant layer (e.g., an Al-oxide), and therefore a strong bias-dependent signal could be observed even in forward direction. Thus the bias dependence in forward direction may give the possibility to observe the build-up of such a layer in situ and thus might be important for understanding the processes leading to the degradation of the diode.

5. Summary

We demonstrated the application of the EFISH technique to organic semiconductor devices. The ITO/PPV/Al diodes show a second-harmonic signal that depends quadratically on the applied bias as can be explained by a simple model. The measured signal mainly reflects the voltage drop over the depletion region of the Schottky contact at the Al/PPV interface. The EFISH technique may be helpful for the in situ investigation of electrical properties of the diodes such as charge trapping effects with high time resolution. It may be also useful for the observation of ageing processes at the PPV/Al interface that are responsible for the degeneration of the diode.

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