Optical Spectroscopy of Field-Induced Charge in Poly(3-hexyl thienylene) Metal-Insulator-Semiconductor Structures: Evidence for Polarons

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We have fabricated metal-insulator-semiconductor structures with poly(3-hexyl thienylene) as the active semiconductor. Optical-absorption bands due to injected carriers seen near 0.4, 1.80, and 2.16 eV are assigned to the optical transitions of the singly charged polaron, which is expected to be the thermodynamically favored excitation under these experimental conditions. Additional absorption bands at 0.5 and 1.18 eV are assigned to optical transitions of doubly charged bipolarons. We contrast the strong confinement deduced for the polaron (gap states separated by 1.80 eV) with the weak confinement observed for bipolarons (gap states separated by 0.7 eV).

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Interest in the semiconductor properties of conjugated polymers is related to the nonlinear electronic response of the coupled electron-lattice system.[1] Charges added to the polymer chain do not reside in band states, but instead form self-localized polaronlike defects with associated quantum states deep within the semiconductor gap. These excitations can take the form of soliton or polaron depending on the symmetry of the polymer backbone. Charge injection in semiconductor device structures provides a novel means for introducing charged excitations into a conjugated polymer (otherwise achieved by chemical doping or photoexcitation of electron-hole pairs). It offers considerable advantages; charge is injected into the polymer without associated counterions, and the charge concentration is both readily controlled and quantitatively established from the device geometry. For the case of *trans*-polyacetylene, which has a degenerate ground state, measurements on the metal-insulator-semiconductor (MIS) and field-effect-transistor (FET) structures have shown that charge injected into accumulation and inversion layers is stored in "midgap" solitonlike states.[2] These measurements involve the detection of the modulation of optical properties of the active layer of the polymer semiconductor in response to a bias voltage applied to the device and can be used to observe optical absorption due to the electronic and vibrational excitations of the charged soliton,[2] and also Raman scattering due to the amplitude vibrational mode of the soliton.[3,4]

Conjugated polymers with a preferred sense of bond alternation support polaronlike self-localized excitations,[5,6] the various states of which are shown schematically in Fig. 1. The charged forms of these are the singly charged polaron ($P^{\pm}$) and the doubly charged bipolaron ($BP^{2\pm}$). Most of the existing experimental measurements on chemical doping[7] and photoinduced absorption[8,9] reveal the presence of bipolarons, and there is at present little direct evidence for the polaron and hence considerable uncertainty as to the positions of the localized states within the gap. Although the bipolaron is expected to be the energetically favored species,[6] for the low concentration of charge present within the accumulation layer of an MIS structure (approximately one charge per 1000 monomer units), the increase in configurational entropy through the $BP^{2\pm} \rightarrow P^{\pm} + P^{\pm}$ process should favor complete dissociation of bipolarons into polarons at room temperature for any reasonable estimate of the bipolaron binding energy (e.g., 0.3 eV).[7] We note that the conditions here are very different from those achieved with chemical doping, for which the role of the counterion is considered to be important; it is likely to stabilize the bipolaron by providing screening of the

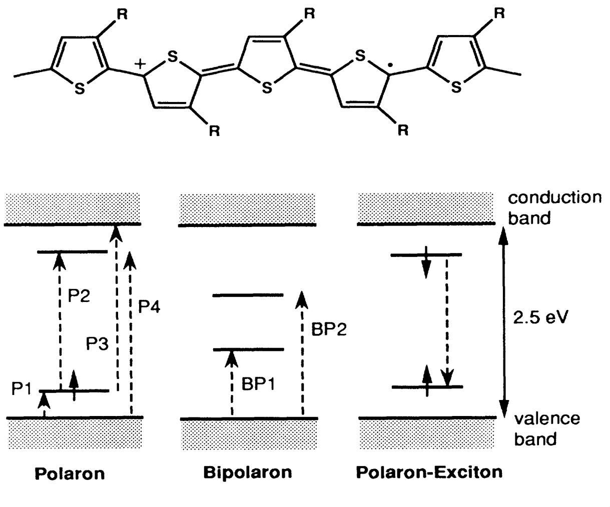

FIG. 1. Schematic diagram showing a positively charged polaron on an alkylthienylene chain. The energy-level scheme and optical transitions for the positively charged polaron and bipolaron, and for the neutral polaron exciton (in its singlet state). Energy levels are as indicated from the present measurements for P3HT.

two like charges, and also through the strain energy associated with separation of the polymer chains to accommodate these ions. We also note that photoinduced-absorption experiments detect long-lived excitations, and that bipolarons, being less mobile and hence longer lived than polarons, are preferentially detected.

We have used poly(3-hexyl thienylene), P3HT, prepared by oxidative coupling of the monomer units, and subsequent reduction to the neutral state.[9] This is a solution-processible polymer, and is thus convenient for device fabrication. The thin uniform films required for MIS devices were obtained by spin-coating P3HT from solution in chloroform. Polymer film thicknesses were chosen to be in the range 50–100 nm—sufficiently thin to allow optical-transmission measurements in the region of the π to π^* absorption band. For infrared measurements, the structures were built with silicon/silicon-dioxide substrates[2] and in the near ir and the visible we used a wide-field spectrosil (WFS) substrate with a partially transparent metal gate electrode, onto which was deposited a thin layer (110–140 nm) of silicon nitride (Si_3N_4) by plasma-enhanced chemical vapor deposition. The Ohmic contact on top of the polymer layer was made with a thin evaporated film of gold.

The formation of a charge accumulation layer for negative bias voltages and charge depletion for positive bias can be demonstrated through the variation of the device capacitance C with bias voltage,[10] and a clear transition from depletion (low capacitance) to accumulation (high capacitance) is observed. From the variation of C with bias voltage in the depletion regime, we estimate the extrinsic charge concentration N_A to be in the range 10^{16}–10^{17} cm^{-3}.[11] There are two sources for these extrinsic carriers: first, through incomplete reduction of the polymer from the oxidized state in which it is prepared, and second, through oxygen doping during sample preparation in air (after *in situ* annealing under vacuum, the extrinsic charge concentration was found to increase on subsequent exposure of the sample to air).

For modulated-absorption measurements covering the range 0.45–3 eV, the premonochromated output from a tungsten lamp was used as the probe and the sample response was measured with Si, Ge, and InAs detectors, using standard phase-sensitive techniques. Both the "in-phase" and "quadrature" responses of the lock-in amplifier were recorded, permitting phase manipulation of the data, and hence the separation of signals with differing phase responses to the applied modulation. Where possible, the bias dependence of the modulated-absorption features were measured, though the scope for this was limited by hysteresis in threshold voltage due to dopant-ion migration.[11] A Fourier-transform infrared (FTIR) spectrometer was used to cover the frequency range 0.05–0.5 eV. Fractional changes in the infrared transmission were measured in response to an applied (dc) bias, and successive bias-on and bias-off cycles were signal averaged until the signal-to-noise ratio was sufficient to obtain the net change in transmittance $\Delta T/T$ (typically 100000 scans, lasting 72 h).

Voltage-modulated transmission can arise from several distinct processes within the material. First, at and above the band edge we expect to see electromodulation of the absorption in response to the instantaneous electric field. Second, we expect to see reorganization of the band quantum states due to the self-localization of the injected charge. This will respond to the instantaneous charge distribution, and will thus be sensitive to the characteristic time constants for charge injection into the device. With careful selection of the frequency of voltage modulation, these two contributions to the overall voltage-modulated transmission spectrum can be separated by analysis of the signal phase information. Third, if experimental conditions allow detection of photoluminescence, we can expect to see variation of the luminescence signal with the charge concentration in the accumulation layer.[12,13] Potential problems encountered in experiments of this type can arise from modulation of interference phenomena and Joule heating. Neither

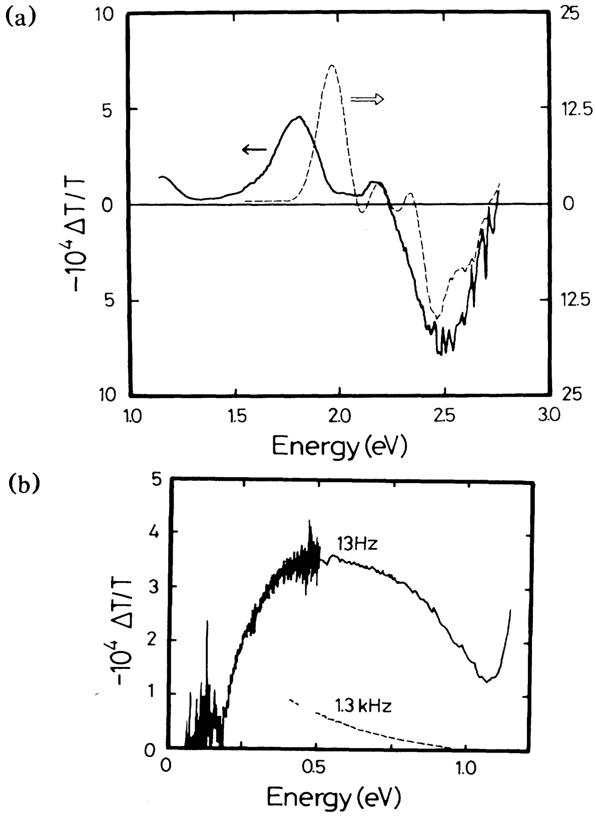

FIG. 2. Voltage-modulated optical-absorption spectra, showing the fractional change in optical transmission $-\Delta T/T$ as a function of photon energy. (a) The electromodulation of the absorption band (data on right-hand scale) and the absorption produced by charge injection (data on left-hand scale) above 1 eV. (b) The absorption produced by charge injection in the ir.

were present in our experiments.

Figure 2(a) shows the room-temperature electroabsorption spectrum for P3HT, obtained using a silicon-nitride/WFS substrate. A 40-V, 390-Hz sinusoidal modulation was applied at zero bias (corresponding to the flat-band condition due to the dopant diffusion), and the signal detected at twice the modulation frequency. The observed response, with strong oscillations due to vibronic transitions, is similar to that reported elsewhere.[14,15] Figure 2 also shows the full injected-charge absorption spectrum at 300 K. Experimental data in the range 1–3 eV, Fig. 2(a), were obtained using an identical sample structure as for the electroabsorption measurements, but with a 20-V, 13-Hz modulation applied over a range of bias voltages, and signal detection at the modulation frequency. Measurements in the infrared, 0.05–1.1 eV, shown in Fig. 2(b), were made on a device built on a heavily doped ($>10^{19}$ cm^{-3}, to give metallic behavior) *n*-Si/SiO$_2$ substrate. A 40-V, 13-Hz modulation, applied at zero bias, was used in the near ir (0.5–1.1 eV), and the spectrum below 0.5 eV was obtained using the FTIR spectrometer, with bias stepped between 0 and -30 V. The spectra were scaled to allow for the different modulation voltages. The most prominent features are the broad electronic transition resolved at 1.8 eV, and the associated bleaching beyond the energy gap (peaking at 2.45 eV). Further subgap transitions are identified at 1.18 and 2.16 eV, and a broad band below 1 eV which we find consists of two features with differing frequency responses, one in the range 0.5–0.6 eV and the other weaker absorption below 0.45 eV. Modulated photoluminescence is shown in Fig. 3. We find that there is a small bleaching in the luminescence signal, which saturates with (negative) bias at about 5%. We attribute this field-induced quenching with nonradiative recombination of singlet polaron excitons at charged polaronic sites,[12] and thus we expect the effect to be confined to the accumulation region. From the thickness of the polymer layer (100 nm) we can thus deduce a value of 5 nm for the width of the accumulation layer.

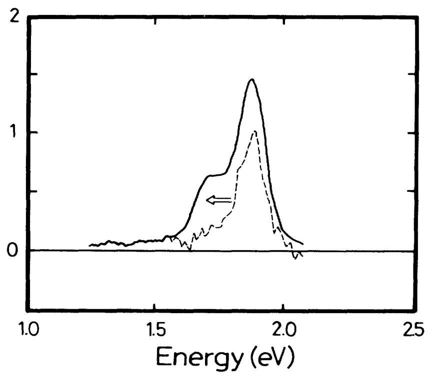

FIG. 3. Photoluminescence spectrum (solid line) and the decrease in photoluminescence on application of a negative bias (dashed line). Excitation was at 514.5 nm, sample temperature 80 K, and the bias was stepped between 0 and -40 V at 310 Hz.

The results presented in Fig. 2 show clear evidence for the creation from band states of states which lie within the semiconductor gap. The question of interest here is whether these gap states are associated with polarons or with bipolarons; the possible optical transitions for these excitations are indicated in Fig. 1. On the basis of their response to frequency and bias voltage, we identify the peaks observed at around 0.5 and at 1.18 eV as being the bipolaron transitions BP1 and BP2 (these energies are similar to those found in photoinduced-absorption measurements[8,9]). The peaks at 1.8 and below 0.45 eV, however, have a different physical origin, and we associate these, together with the weak 2.16-eV absorption just inside the bleaching, with the three electronic transitions of a singly charged polaron as shown in Fig. 1; P1 (<0.45 eV), P3 and P4 (2.16 eV), and P2 (1.8 eV). We note that most of the oscillator strength for the polaron transitions is at energies close to the onset of interband transitions, and it is only through the use of the differential spectroscopy that is possible for the MIS device that we are able to differentiate between these features and the interband response. Information about the spin associated with the excitation is important, and we note a recent report giving evidence for a doublet at 1.8 eV in optically detected magnetic-resonance experiments.[16]

This assignment of the optical-absorption features to polarons and bipolarons does give a picture that is broadly consistent with the thermodynamic equilibrium expected, with a preponderance of polarons at room temperature (we have also seen a relative increase in the "bipolaron" signal at lower temperatures). However, we must be careful to examine the role of extrinsic defects in the stabilization of the injected charges; for the case of polyacetylene there is evidence that the surface layer in which the accumulation charge is stored can be more disordered than in the bulk.[4] For the present experiments, we see from the similar spectral resolution of the bulk and bleached surface-layer photoluminescence (Fig. 3) that the surface layer is not significantly different from the bulk. We do suspect that the bipolarons are extrinsically stabilized; thermodynamic arguments require a very low concentration at room temperature, and we note below that the positions of the gap states are not well modeled.

The degree of confinement of the polaron is conveniently parametrized by the ratio ω_0/Δ, where $2\omega_0$ is the separation between the intragap polaron levels and 2Δ is the energy gap.[6] For the case of bipolarons in P3HT, we observe a splitting of $2\omega_0 \approx 0.7$ eV which, taking the value for the energy gap as $2\Delta \approx 2.5$ eV (the peak in the π to π^* absorption), implies a relatively weak confinement parameter. As reported for photoinduced absorption and doping of P3HT,[6,7,17] the peaks of the two bipolaron transitions are asymmetrically displaced about the midgap. This can be explained by the addition of a Coulomb interaction within a perturbation framework.[18,19] As applied to polarons, the Coulomb interaction does not affect the P1 and P2 transitions but splits the P3-P4 transition into a triplet,[20] and we have therefore used the one-electron energies for these transitions. This assignment sets $2\omega_0$ equal to 1.8 eV. We note that this value of $2\omega_0$ is similar to that obtained for the polaron exciton deduced from the energy of the photoluminescence (1.7 eV). The relative positions of the gap states for these excitations are indicated in Fig. 1. The value of ω_0/Δ for the polaron or polaron exciton gives, with the model of Fesser, Bishop, and Campbell,[6] a large value for the confinement parameter γ of about 0.8. γ is defined by the relation $\gamma = \Delta_e/\Delta\lambda$, where Δ_e is the extrinsic contribution to the energy gap and λ is the electron-phonon coupling constant, and we emphasize that a value for γ of order 1 is expected from reasonable estimates for these parameters. We consider that the very small values of confinement parameter deduced for bipolarons in these and other polymers[21] are poorly understood, and note that the recent calculations of Choi and Rice[22] go some way towards resolving this issue.

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