The photovoltaic response in poly(*p*-phenylene vinylene) thin-film devices

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Abstract. We report measurements of the photovoltaic effect in diode structures formed with thin films (100 nm) of the conjugated polymer poly(*p*-phenylene vinylene), PPV, sandwiched between electrodes of indium/tin oxide, ITO, and either aluminium, magnesium or calcium. Under illumination incident through the ITO contact, large open-circuit voltages were measured, which saturated at ~ 1.2 V for Al and Mg devices, and ~ 1.7 V for Ca devices. Quantum efficiencies (short-circuit current/incident photon flux) of order 1% were measured at low intensities (0.1 mW cm^{-2}). The spectral response of the photocurrent demonstrates that photon absorption near the electron-collecting electrode optimizes the photocurrent, indicating that device performance is limited by low electron mobilities in the bulk PPV. The photocurrent exhibits a weak temperature dependence, with an activation energy that is a function of the electric field in the polymer. We have used these measurements to estimate an exciton binding energy in PPV of ~ 0.4 eV.

1. Introduction

The semiconducting properties of conjugated polymers derive from the delocalized π conduction and valence bands formed by overlap of p_z orbitals at each site along the polymer chain. Bandwidths can be several electron volts, and high electron mobilities are achieved when these materials are chemically doped to achieve partial filling of the conduction or valence band [1]. Since the early interest in the electronic properties of these materials in the late 1970s, methods for processing these polymers have been developed to the point where they are now used in a range of applications, largely as processible conductors [2].

Conjugated polymers exhibit a range of interesting properties as semiconductors. Coupling of the excited electronic configuration to the local geometry of the polymer chain results in spatial localization of excitations within individual polymer chains. These polaronic excitations are considered to occur as singly charged polarons, doubly charged bipolarons, and neutral polaron–excitons (both singlet and triplet) [3–6]. One of the effects of this localization of the excited-state wavefunction is that the binding energy of the singlet exciton is considerably larger than that for inorganic semiconductors, being larger than kT at room temperature, so polymers that are free of quenching centres can show high photoluminescence efficiencies [7–10].

With improvements in polymer processing [11], it has become possible to fabricate a range of thin-film active semiconductor devices, including field-effect transistors [12–15], field-effect electro-optical modulators [16], and light-emitting diodes, LEDs [17–21]. There is particular interest in polymeric LEDs since there is no widely used large-area thin-film technology based on other materials at present, and recent improvements in device

performance have raised efficiencies to several percent [22]. Alongside the interest in developing devices that may be of technological interest, these structures have also provided an important experimental tool for investigating the behaviour of excited states introduced into the polymer under controlled conditions. For example, measurements of modulation of optical absorption in response to modulation of the device operating voltages allows measurement of charged polarons [12, 23, 24] and also triplet excitons [25]. We present here a detailed study of the photovoltaic response of some diode structures that are very similar to those used as LEDs, and use the results to obtain basic information about the semiconductor properties of the polymer used, poly(*p*-phenylene vinylene), PPV, the chemical structure of which is shown in figure 1.
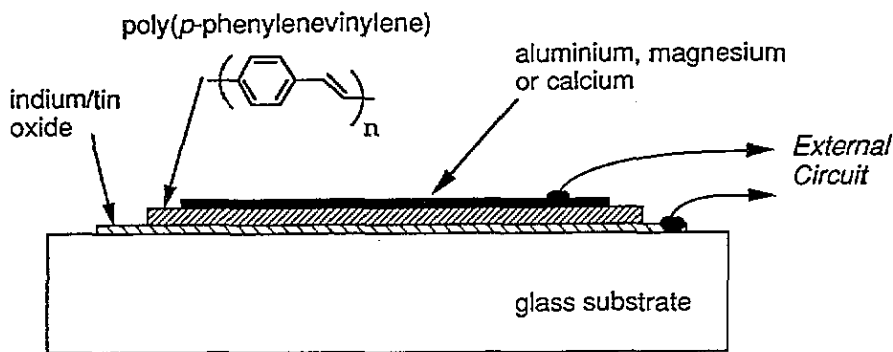

Figure 1. Schematic diagram of the structure of the PPV photodiodes used in this work.

There has been interest in the photovoltaic properties of molecular semiconductors over many years, see for example [26], but devices made with semiconductors of this type tend *not to show useful efficiencies. There are several reasons for this, of which the difficulty* in achieving efficient ionization of the excitons initially created by photon absorption is probably the most important, though poor electron or hole mobilities are also problematic. Ionization of excitons that have binding energies significantly above kT can be achieved in the bulk (as is the case for the PPV-based devices reported here), but is often facilitated by the presence of a surface or interface. At a heterojunction between molecular semiconductors with differing electronegativities, ionization to place electrons in one layer and holes in the other can be arranged to be energetically favoured, and some of the best photovoltaic responses have been obtained from devices of this type [27]. We mention also that interest in the organics has been recently revived by the work of O'Regan and Grätzel [28], who fabricated a photoelectrochemical cell with electron–hole separation in an organic dye, electron transfer to a TiO_2 substrate and hole transfer to reduce iodide ions in solution. This cell offers high efficiency (energy efficiency up to 12% in diffuse sunlight).

Conjugated polymers were, of course, put into photocells at an early stage, but did not produce very promising results, with relatively low open-circuit voltages and low overall efficiencies. Initial efforts were with polyacetylene [29, 30] and some of the polythiophenes [31, 32]. The low open-circuit voltages were attributed in part to the efforts of polaron formation, *which appear to move one-electron levels deep into the semiconductor gap*, so that the energy difference between the energies of the one-electron hole and electron levels can be very much smaller than the π–π^* energy gap. The extreme case is that

of *trans*-polyacetylene, where the excitations take the form of solitons with non-bonding levels at mid-gap, and which can be either positively or negatively charged, so that the one-electron levels for electrons and holes are coincident [33]. The chemical potential for these carriers must also take the lattice polarization into account, so that larger photovoltages can be produced [13, 34]. The discovery of electroluminescence in conjugated polymers such as PPV [17], which results from capture of positive and negative polarons to form singlet excitons, which then decay radiatively, prompts a re-examination of the energetics of polaron formation in these polymers. In particular, the singlet exciton emission is close to the onset of $\pi-\pi^*$ absorption [35, 36] and since this exciton is created from positive and negative polarons, the free energy of these two charged states cannot be much smaller than that of the singlet exciton. This requires that the movement of the polaron states into the gap is very much less pronounced under the conditions of charge injection in devices of this type than had been inferred from the optical spectroscopy of chemically doped polymers. As we report here, we find that the open-circuit voltages of the photovoltaic cells constructed with polymers such as PPV can be very large, approaching the difference in work function between the two electrodes in some cases.

PPV, the polymer used in the present work, can be conveniently processed via soluble precursor polymer to form thin films of high uniformity [11, 17, 19, 37–39], and together with its relatively high luminescence efficiency, this has led to its use as the material of reference for work on polymer LEDs. The first $\pi-\pi^*$ optical absorption is just below 2.5 eV, and the balance of evidence is that it is due to the $(0, 0)$ vibronic transition to the vibrational ground state of the singlet exciton [35, 40]. Photoluminescence from the radiative decay of the singlet exciton appears at the $(0, 0)$ transition just below the $\pi-\pi^*$ absorption edge, and in a series of vibronic bands red-shifted from the $(0, 0)$ emission. Photoexcitation from π to π^* states results primarily in the formation of intra-chain singlet excitons, but the formation of triplet excitons is also seen [41, 42], and there is evidence from optically detected magnetic resonance experiments for the transient presence of spin-$\frac{1}{2}$ charged excitations, which later produce singlet emission, by electron–hole capture to re-form the singlet exciton [43]. Generation of charged excited states can be observed by measurements of photoconductivity, and this has been reported by several groups [42, 44–49]. For measurements with current flow within the plane of the polymer film, the steady-state photocurrent shows a sub-linear dependence on light intensity, indicating that there is bimolecular recombination of positive and negative charges. The spectral dependence of the photoconductivity shows a strong onset at the $\pi-\pi^*$ absorption edge at 2.5 eV, and increases at higher photon energies for thin samples [42]. For thicker samples the action spectrum peaks close to this onset, at the wavelength where photon absorption occurs through the full thickness of the sample. Further into the absorption edge, as the absorption depth falls well below the film thickness, the photocurrent falls on account of increased bimolecular recombination [44, 45, 50]. These results have been taken to indicate that photogeneration of carriers in PPV occurs principally in the bulk [42].

2. Experimental details

PPV films of thickness of order 100 nm were prepared via the sulphonium salt precursor route, by spin-coating films of the precursor polymer from solution in methanol onto the ITO-coated glass substrates. Conversion to PPV was achieved by heating *in vacuo* at 250 °C for 4 h. Top metal contacts were subsequently deposited by thermal evaporation. The Al and Mg devices had an active area of 2 mm^2, and the Ca devices 1 mm^2. Handling of the

Ca devices was carried out in a glove box, prior to encapsulation with an epoxy resin to prevent corrosion in air.

The choice of the precursor polymer and conversion protocol has considerable influence on the electronic properties of the PPV produced. It is considered that relative strengths of the vibronic transitions in the $\pi-\pi^*$ absorption band are sensitive to the degree of intra-chain order, which can be increased by modification of the precursor polymer [42, 48], or by ordering on an orienting substrate [51]. However, for the work presented here, we have used the standard precursor route, with the tetrahydrothiophene leaving group, as used in the fabrication of PPV-based LEDs [11, 17, 20, 52].

The diodes were mounted in a continuous-flow helium cryostat provided with optical windows. For measurements of the current–voltage characteristics the devices were illuminated by light, from the ITO side unless otherwise stated, from an argon ion laser at either 457.9 nm or 496.5 nm, and the intensity was controlled with neutral-density filters. A Keithley 230 voltage source was used to drive the devices, and a Keithley 617 electrometer monitored the current through the device by measuring the voltage across a shunt resistor, which was chosen to be small compared with the device resistance at that bias.

Measurements of the spectral response were made by illuminating the diodes with light from a tungsten lamp source, passed through a Chromex 250/500 monochromator. The circuit mentioned above was used to bias the sample. These measurements were corrected for the response of the lamp–monochromator system, by measuring the spectral response of a silicon photodiode placed in the sample position.

3. Results

3.1. Current–voltage characteristics

Current–voltage ($I–V$) characteristics of an ITO–PPV–Mg diode (PPV layer of thickness 120 nm) in the dark and under laser illumination at 496 nm are shown in figure 2. The device is strongly rectifying in the dark, but under illumination a substantial open-circuit voltage is observed, and current flow is enhanced in both forward (ITO held positive) and reverse bias. The open-circuit voltage of this device is plotted as a function of incident intensity in figure 3, where it can be seen that the voltage rises steeply at low intensities before saturating at around 1.2 V. The $I–V$ characteristics of devices made with Al and Ca were qualitatively similar, and the maximum photovoltages obtained are listed in table 1. The fill factor of the similar, and the maximum photovoltages obtained are listed in table 1. The fill factor of the $I–V$ curves is about 0.2, which is a common figure for organic photodiodes, but small compared to the best devices available [27].

Table 1. The expected and measured maximum photovoltages obtained with ITO-PPV-metal photovoltaic devices.

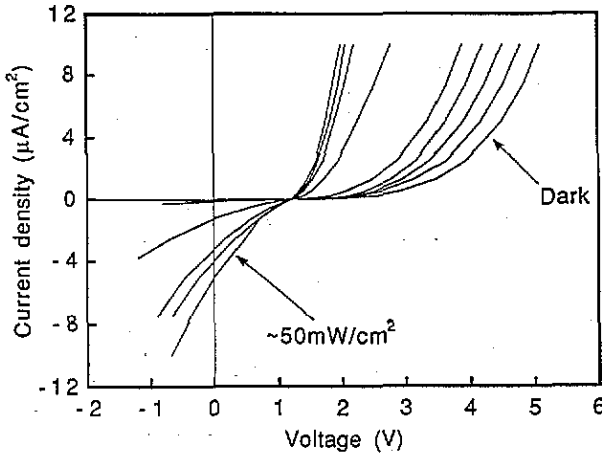| Metal contact used	Measured maximum photovoltage (V)	Metal work function (eV)	Difference in work function with respect to ITO (V)
Aluminium	1.2	4.28	0.5
Magnesium	1.2	3.66	1.2
Calcium	1.7	2.87	1.9

Figure 2. *I–V* curves for an ITO–PPV–Mg device, with PPV layer of thickness 1200 Å, illuminated by 496 nm radiation from an Ar$^+$ laser.
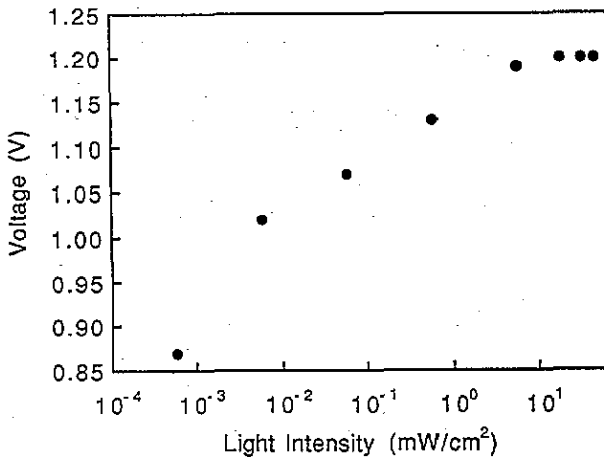

Figure 3. The open-circuit voltage developed across the device of figure 1, as a function of incident intensity.

As the field inside the PPV rises, the current through the device rises well above the dark current, both in forward and reverse bias. This is shown very clearly in the *I–V* characteristics under strong forward bias, as shown for an ITO–PPV–Mg device (PPV layer thickness 220 nm) in figure 4. We define the photoconductive gain as the ratio of the number of charges collected in the external circuit to photons incident on the device, and the gain at an incident photon flux of 70 μW cm^{-2} is shown in figure 5. note that this rises to values greater than unity, which requires that the lifetime of the photocarriers is greater than their transit time across the device, so that each carrier can make several effective crossings of the PPV layer [53].

The variation of the short-circuit current with intensity for devices with Al, Mg and Ca contacts is illustrated in figure 6 for excitation at 457.9 nm. The photocurrent for the three
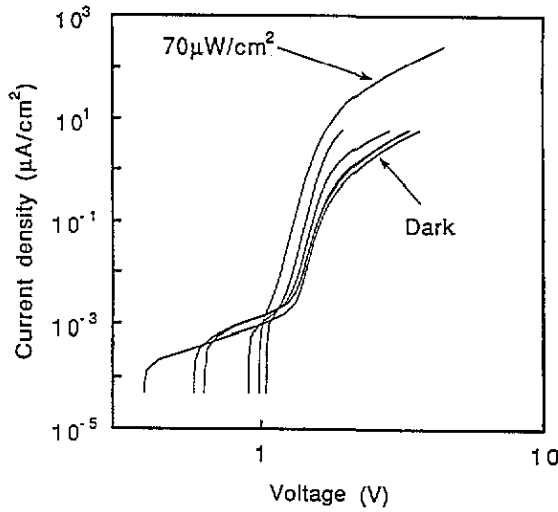
Figure 4. *I–V* curves of an ITO–PPV–Mg device at high forward bias, illuminated at 496 nm.
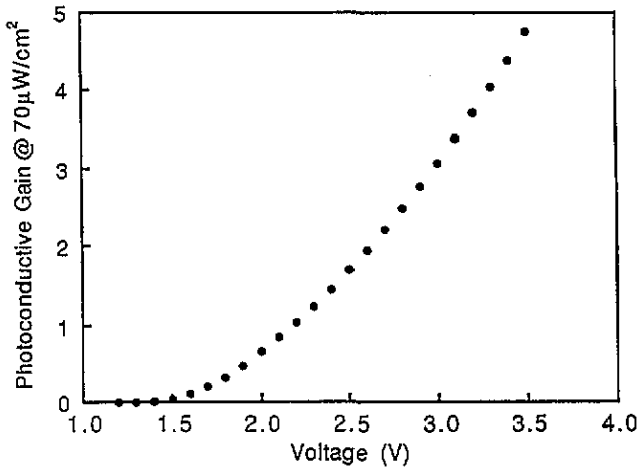

Figure 5. The variation of the photoconductive gain (the ratio of the number of charges collected in the external circuit to photons incident on the device) with bias voltage at an incident photon flux of 70 μW cm^{-2}.

devices follows an approximately sublinear power law, $J \propto L^{\kappa}$, with an exponent κ of around 0.8 at higher intensities. The PPV layer thicknesses for the Al, Mg and Ca devices were 110, 50 and 320 nm respectively, and we expect that much of the variation in efficiency between these devices is due to the differing polymer layer thicknesses. The quantum yield, defined as the ratio of the measured short-circuit photocurrent to the estimated photon flux incident on the diode, was measured for a range of devices. System calibration was performed by replacing the PPV photodiode with a silicon photodiode of known efficiency, but no corrections were made for reflectivity at the device interface. Quantum yields for devices made with Mg as the electronegative electrode were found to vary systematically

with the thickness of the PPV layer, with typical values of 1% for PPV layers of thickness 50 nm, and 0.5% at 90 nm for power levels of 0.1 mW cm^{-2}.
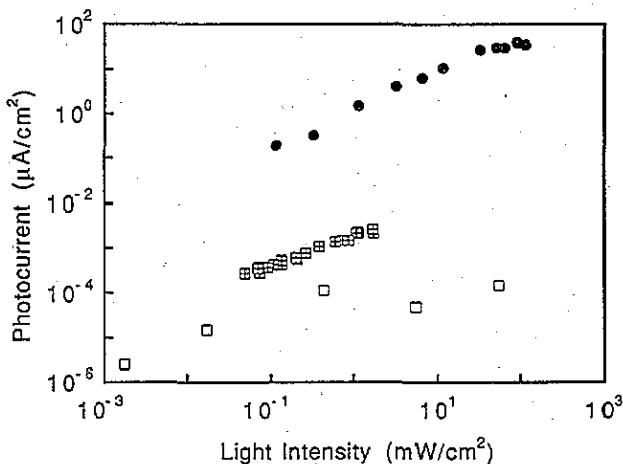

Figure 6. The short-circuit current of ITO–PPV–metal diodes: open squares, ITO–PPV–Al (110 nm); filled circles, ITO–PPV–Mg (50 nm); hatched squares, ITO–PPV–Ca (320 nm). The anomalous behaviour of the two data points at the highest intensities shown for the Al device may be due to partial breakdown of the diode.
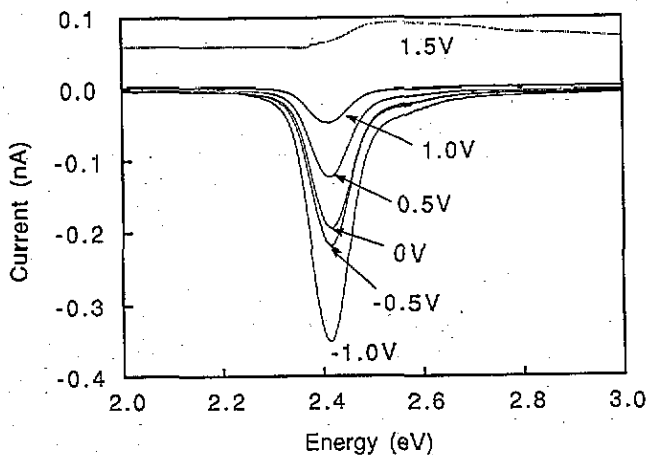

Figure 7. The spectral response of the current through an ITO–PPV–Mg diode, with PPV layer thickness 200 nm, for a range of applied voltages (device thickness 220 nm). These data have not been corrected for the dark current, the spectral response of the light source and monochromator or the device reflectivity.

3.2. Spectral dependence

The spectral response of the current for an ITO–PPV–Mg device with a relatively thick layer of PPV (220 nm) is shown in figure 7 at biases between −1.0 V and +1.5 V. No correction has been made for the response of the light source and monochromator, or for reflectance from the device. The spectra show a sharp peak at the onset of the optical gap (about 2.5 eV), and a shallower tail at higher photon energies. Between 1.0 and 1.5 V the polarity of the photocurrent reverses, which indicates that the polarity of the electric field inside the device has reversed between these voltages. This is consistent with the open-circuit voltage for Mg diodes of 1.2 V shown in figure 3. Figure 8 shows the same data, after the dark current has been subtracted, the photocurrent corrected for the lamp–monochromator response and the peak photocurrent normalized to unity. The broken curve is the normalized absorption spectrum of PPV, shown for comparison. The spectral response at 1.0 V and below is independent of field, although its magnitude varies by an order of magnitude as shown in figure 7. However, the response at 1.5 V is very different; the peak energy is blue-shifted, and the high-energy photon response is much improved.
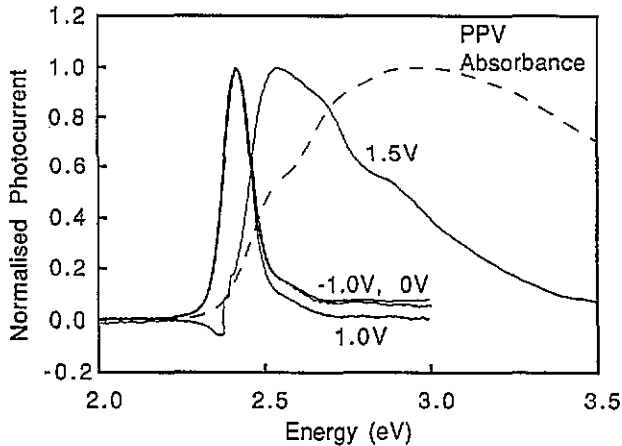

Figure 8. The data shown in figure 5 after correction for the dark current, light source and monochromator response, and normalization to the same peak value. The broken line is the normalized absorption spectrum of PPV, measured as −log(transmission).

The spectral response of the short-circuit current was measured for devices with a range of PPV layer thicknesses, as shown in figure 9. The data were taken at room temperature, and were normalized according to the procedure used for the 220 nm thick device shown in figure 8. The peak broadens and shifts to higher photon energies as the thickness of the PPV film decreases. The spectral response of the short-circuit current is fairly insensitive to temperature below about 300 K, but above this temperature the peak position shifts to a higher energy and the peak broadens. The energy of the peak position is plotted against temperature in figure 10.

An ITO–PPV–Al device was constructed with a semi-transparent Al contact so that the device could be illuminated from either side of the sample. The Al layer showed a transmittance of approximately 50%. Figure 11 compares the spectral response of the diode current when illuminated through the ITO in short circuit and with 1.5 V applied bias, and
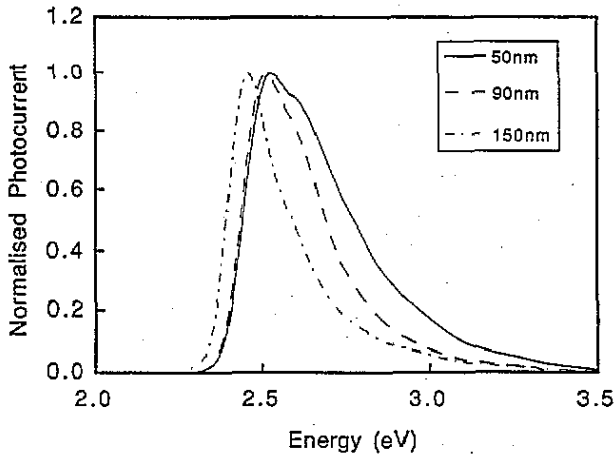
Figure 9. The spectral responses of ITO–PPV–Mg diodes with different PPV layer thickness.
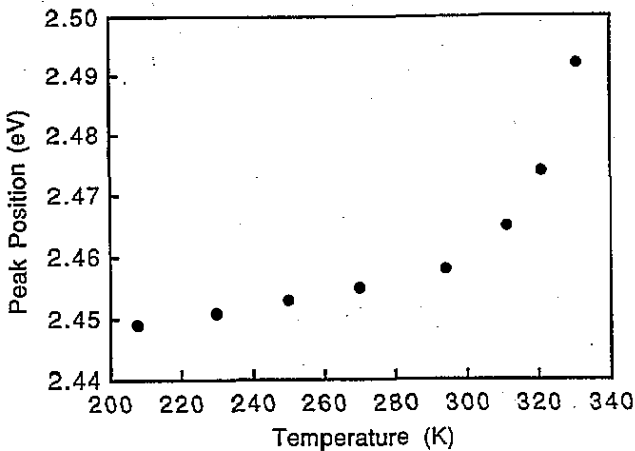
Figure 10. Photon energy at the peak of the photovoltaic response shown as a function of device temperature.

that of the short-circuit current when illuminated through the Al. The broken line is the normalized absorption spectrum of PPV and is shown for comparison. The response of the diode when illuminated through the Al is slightly different from that when illuminated through the ITO with a 1.5 V bias applied, with the high-photon-energy response slightly stronger, and with more vibronic structure visible.

Figure 12 shows the variation of short-circuit photocurrent of a 130 nm device with temperature, for several biases. The solid lines are experimental data, and the broken lines are exponential curve fits to these data. The devices were illuminated at 496.5 nm, and were cooled at a rate of approximately 0.5 K min^{-1}. The curves show an approximate Arrhenius form, $J \propto \exp(-E_A/kT)$, with a bias-dependent activation energy E_A. The activation energies obtained were 0.067 eV (0.0 V bias, cooling), 0.12 eV (0.5 V bias, cooling), 0.22 eV (0.5 V bias, warming) and 0.36 eV (1.0 V bias, warming). The two
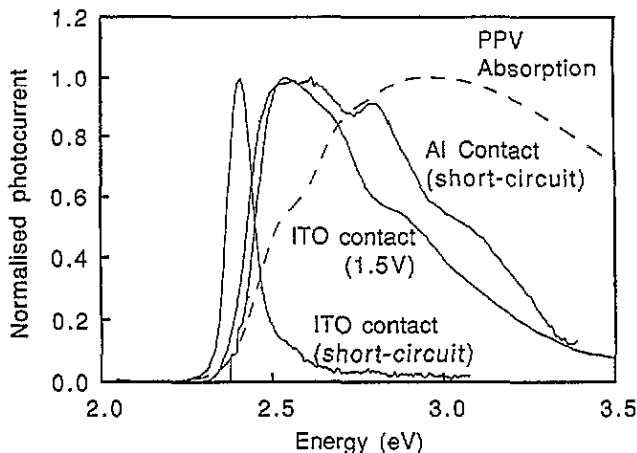
Figure 11. Comparison between the spectral response of an ITO-PPV–Al diode when illuminated through the ITO contact and the semi-transparent Al contact. The responses at 0.0 V and 1.0 V bias are shown for the ITO case. The data were normalized as in figure 6.

different activation energies at a bias of 0.5 V indicate that the cooling or heating may not have been at equilibrium. Measurements of the temperature dependence of the short-circuit current were made for two ITP-PPV–Mg devices, with thicknesses 1300 Å and 500 Å. These gave activation energies of 0.058 eV and 0.036 eV respectively.

4. Discussion

4.1. Background

The generation of substantial photocurrents and large open-circuit voltages in these photodiodes indicates that charge generation following photoexcitation can be an important process in PPV. Our results are in this respect consistent with those obtained by the Bayreuth [39, 54] and Xerox [55] groups. We note also that photovoltaic responses have been reported for heterostructure diodes with a soluble derivative of PPV and fullerene used for collection of holes and electrons respectively [56]. We remark that PPV has a very low dark carrier density, and that therefore Schottky barriers are not expected to form at the interfaces with the electrodes. For the diodes we have investigated here, the ITO electrode has the higher work function, and will be biased positive with respect to the other electrode under open circuit. As the potential across the diode is reduced towards zero and to negative values, substantial internal fields are generated within the PPV layer, which act to pull holes *towards the ITO contact and electrons towards the other electrode, and we note that under* short-circuit conditions, with the high open-circuit voltages and thin PPV films used, an internal filed of order 10^5 V cm^{-1} is present. These fields may certainly assist in the separation of photogenerated charges.

PPV as prepared according to the methods we have employed here and also for the construction of LED devices is highly insulating, with a dark conductivity of 10^{-12} S cm^{-1} or lower. Charge carriers are present in the dark at a concentration that is too low to allow direct characterization of their properties, but we consider that they are p type since carriers of this type are found in materials that show higher levels of conductivity, sufficient to allow
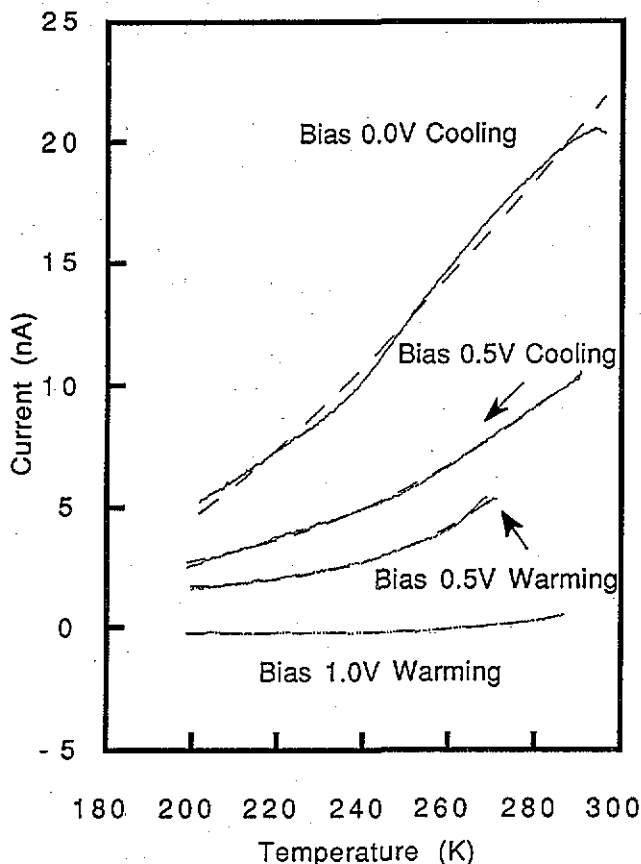
Figure 12. The temperature dependence of the photocurrent in an ITO–PPV–Mg device (thickness 130 nm) as a function of applied bias. The solid lines are the experimental data, and the dashed lines are exponential curve fits.

formation of depletion layers of variable width in Schottky barriers formed with low-work-function metals, or in metal–insulator–semiconductor field-effect diodes. In particular, we find that dialkoxy-substituted PPVs, which possess a lower band-gap than PPV, show good p-type extrinsic behaviour with carrier concentrations deduced from capacitance versus bias voltage characteristics of order 10^{17} cm^{-3} [24].

Carrier mobilities in PPV have been measured by time-of-flight techniques, and these indicate a hole mobility of order 10^{-4} cm^2 V^{-1} s^{-1} at room temperature [45, 46]. The hole mobility in PPV, which had not been fully converted from the precursor polymer, has been measured at 10^{-5} cm^2 V^{-1} s^{-1} at an applied field of 10^5 V cm^{-1} at room temperature [57]. In the latter measurement current transients were no longer discernable in fully converted PPV, indicating very dispersive transport of holes and considerable trapping. There are no reports of electron transients, but from the smaller magnitude of the photocurrents under appropriate bias, it is concluded that electron mobilities are some two orders of magnitude lower. This lower electron mobility must result from the presence of traps, probably due to oxygen incorporated in the PPV film, since the π and π^* valence and conduction bands are very similar in width [58] and should thus give rise to similar electron and hole mobilities.

We consider that extrinsic charge carriers play little part in the photovoltaic response of the photodiodes studied here. We do not consider that either the dark or illuminated $I-V$ characteristics can be accounted for by a model for a Schottky barrier at the illuminated contact. Under dark conditions, passage of charge across a PPV diode of this type takes place by injection of charge across barriers at the polymer–electrode interfaces. The hole current is considered to be dominant since holes are the higher-mobility carriers, and since also most of the devices that have been studied to date use metals for the cathode that present a larger barrier for electron injection than for the holes from the ITO electrodes. Injection by means of thermionic emission over the barrier appears to be dominant at room temperature, but tunnelling through the barrier may be more important at lower temperature.

We note however that PPV prepared by the Bayreuth group appears to be considerably more conducting that the material we have used here, and that the properties of the devices that this group have studied can be modelled by considering a Schottky junction at the cathode [39, 54]. Analysis of the variation of the depletion layer width with bias voltage gives an extrinsic hole concentration as high as 10^{17} cm^{-3} [54].

4.2. Open-circuit voltages

We consider that if there are no interfacial layers between the metal electrodes and the PPV layer that the limit to the photovoltage in each case should be set either by the difference in the work function between the two metal electrodes, or by the difference between the free energies of the positive and negative polarons, whichever is the smaller. We also list in table 1 the difference in work function between ITO and the metal in question, taking a value for the ITO work function of 4.8 eV (the work function of ITO is a function of the manufacturing conditions, but is expected to lie between 4.5 and 5.0 eV). The Al, Mg and Ca work functions are based on photoelectric emission experiments [59–61]. The measured photovoltages for Mg and Ca devices approximately scale with the metal work function, whereas the photovoltage measured in Al devices is clearly larger than that expected from the work function difference of the contact materials. The reason for this is unclear, but we note that the surface layer of Al reacts with PPV to form covalent bonds across the vinylene linkages, thereby introducing a non-conjugated barrier layer [62].

4.3. Spectral dependence of the photocurrent

The spectral response can be interpreted by a model involving the mean range of electrons and holes (the average distance travelled before a recombination or trapping event), if the mean range of holes is much greater than that of electrons. As discussed in section 4.1 above, there is clear evidence for such a disparity in carrier mobilities. When light at wavelengths above the absorption edge of PPV is incident on the ITO electrode, it is absorbed in the PPV layer close to the ITO contact. In short circuit, the internal field in the PPV is such that electrons travel towards the metal contact and holes towards the ITO contact, so if the thickness of the unilluminated region of the PPV is greater than the mean range of electrons then the response will be small, because very few electrons will be able to traverse the PPV. When the absorption coefficient is small, charges are photoexcited close to the metal electrode, so electrons can escape from the PPV, but little light is absorbed. The spectral response is therefore limited by the competition process between the amount of light absorbed and the location of the absorption region, and the photocurrent peaks at a photon energy that balances these two factors. The thickness of the PPV will strongly affect the position of the peak. As the film thickness drops, the high-energy photon response will improve, so that the photocurrent peaks at a photon energy such that the absorption depth

in the PPV is approximately equal to the thickness of the PPV film. Reducing the polymer layer thickness will also increase the internal electric field in the polymer under short-circuit conditions, and this will further increase the photoconductive gain.

When the polarity of the internal field is reversed by the application of a sufficiently large positive bias, the spectral response changes, as is seen very clearly as the bias is raised from 1 V to 1.5 V for the ITO–PPV–Mg device shown in figures 7 and 8, and for the ITO–PPV–Al device shown in figure 11. At 1.5 V bias, electrons now leave the PPV through the ITO interface, and so it is advantageous for the light to be absorbed close to the ITO interface. The holes are more mobile than the electrons, so a much larger proportion of the photoexcited holes reaches the opposite metal electrode. Therefore the response at higher photon energies is improved when the electric field in the device is reversed. The position of the peak in the response also shifts towards higher energies, for the same reason.

When light is incident on the semi-transparent Al electrode (figure 11), the electric field is oriented such that electrons leave at the illuminated contact, so in this case the response is similar to that when a 1.5 V bias is applied to a device illuminated through the ITO. The reason for the enhanced vibronic structure observed in the case of illumination through the Al contact is unclear. Possible causes include a difference in structure of the PPV close to the ITO and Al contacts, which may influence the local absorption spectra, or differences in the spectral response of the reflectivity at ITO–PPV and Al–PPV interfaces.

The shift in photon energy of the peak photocurrent with temperature, which is seen in figure 10, will result from the temperature dependence of the optical gap and charge mobility in PPV. There is an increase in the π–π^* gap as temperature is increased [42], which is associated with increased amplitude in torsional oscillations of the polymer chain, which reduce the strength of the p_z orbital overlap along the chain. As the temperature rises, the charge mobility is also expected to rise. This will in general increase the mean range of charge carriers, and therefore improve the spectral response of the photodiodes. It is interesting to note that the spectral response changes little below ~ 300 K, although the charge mobility is expected to drop significantly below room temperature.

4.4. Form of the I–V curves

The shape of the *I–V* curves in PPV devices is very different to those of conventional photodiodes, such as those made with silicon [63], in which the photocurrent is superposed on the dark *I–V* curve, since the photocarrier generation efficiency is largely insensitive to the applied bias. If, in PPV devices, carrier generation results from ionization of excitons in the bulk of the polymer, then we can expect that the generation efficiency will be dependent on the electric field present within the PPV. When short-circuited, the reverse bias field inside the PPV is the open-circuit voltage divided by the thickness of the polymer layer, and will be of order 10^5 V cm^{-1} in the devices studied here. The carrier generation efficiency is smallest when a positive bias is applied to the diode to give a flat-band condition inside the PPV, but will then rise as the device is taken into forward bias, as evident in figure 2.

The large increase in current under large bias voltages, both forward and reverse, is interesting, not least because the photoconductive gain can exceed unity (see figure 5) even though the efficiency of generation of charge-carrier pairs from each photon absorbed in the PPV layer is considerably less than unity. This high photoconductive gain indicates that the lifetime for the more mobile photocarrier (here this will be the holes) is greatly in excess of the transit time of these carriers across the device. We consider that the charge pair generation efficiency is probably not much larger than the figure of 1% that we find for the photovoltaic quantum efficiency, and we propose that the lifetime of the photogenerated electrons in the PPV layer is very considerable. During the lifetime of these electrons, holes

can transit across the polymer layer, under forward bias towards the Al, Mg or Ca electrode, and reappear back at the ITO electrode, be re-injected and transit the polymer layer again. At the photoconductive gains shown in figure 5 and assuming a quantum efficiency for charge pair generation of 1%, we thus require that the electron mobility be two to three orders of magnitude lower than that of the holes. We note that a similarly low value for the electron mobility has been deduced from studies of the width of the electron–hole capture region in PPV-based LEDs [64], and from photoconductivity measurements [46].

We have found that the quantum yield for the short-circuit photocurrent is of order 1%. in contrast, yields for charge generation in photoconductive experiments in PPV and related polymers have been reported to be considerably larger, at values of order 25% [49, 65]. It is not clear why there should be such a considerable discrepancy between these values, since in particular, the charge generation experiments of Abkovitz *et al* were arranged to avoid hole injection from the ITO contact [65, 66]. One possibility is that we have not achieved the optimum carrier generation, and we note that we have for some samples measured rather higher quantum efficiencies than we usually obtain.

4.5. Temperature dependence of the photocurrent

The temperature dependence of the photocurrent provides a measure of its activation energy, which was found to be bias dependent, as shown in figure 12. As the applied bias increases from 0 V the internal field drops, because the short-circuit field is in reverse bias. As the internal field drops, the activation energy of the photocurrent rises. When the applied bias is extrapolated to zero internal field, the activation energy is ~ 0.4 eV. This may correspond to the binding energy of the exciton in PPV, and correlates quite well with other recent measurements including luminescence quenching [67] and magnetic-field-dependent photoconductivity experiments [40], which suggest a binding energy of ~ 0.4 eV and ~ 0.3 eV respectively.

5. Conclusions

We have fabricated ITO–PPV–metal photodiodes which exhibit comparatively large open-circuit voltages. Those of Mg and Ca devices approximately scale with the work function of the metal, which may indicate that the PPV–Mg and PPV–Ca interfaces are relatively free from traps. It is not clear why the open-circuit voltage of Al diodes is much larger than its work function would suggest, but it may be related to the chemical reaction that occurs between Al and PPV.

The intensity dependence of the short-circuit current and the spectral response of the photocurrent indicates that bimolecular recombination in the PPV limits the photocurrent. The response can be maximized by reducing the distance the less-mobile carriers (electrons) have to travel before they leave the device.

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