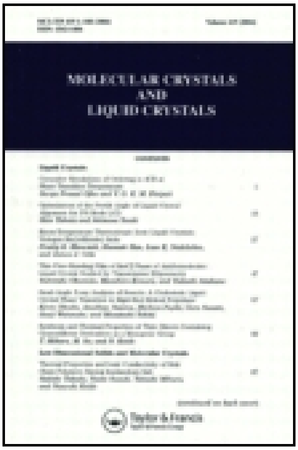

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

A Study of the Charged Excitations in Thin Films of α-Sexithiophene by Voltage-Modulation Spectroscopy and Photoimpedance Measurements

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To cite this article: M. G. Harrison , R. H. Friend , F. Garnier & A. Yassar (1994): A Study of the Charged Excitations in Thin Films of α-Sexithiophene by Voltage-Modulation Spectroscopy and Photoimpedance Measurements, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 252:1, 165-174

To link to this article: http://dx.doi.org/10.1080/10587259408038222

Mol. Cryst. Liq. Cryst. 1994, Vol. 252, pp. 165–174
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Printed in the United States of America

A STUDY OF THE CHARGED EXCITATIONS IN THIN FILMS OF α-SEXITHIOPHENE BY VOLTAGE-MODULATION SPECTROSCOPY AND PHOTOIMPEDANCE MEASUREMENTS

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Abstract We report on the spectra of charged excitations present in solid-state thin films of α-sexithiophene. We use Voltage - Modulation Spectroscopy to charge the oligomer chains electrically by the field effect in Metal - Insulator - Semiconductor (MIS) devices in which α-sexithiophene is the active semiconductor layer. This technique allows us to probe the charged excitations in a solid state thin film device environment, whilst avoiding the steric and coulombic perturbations due to counter-ions present in chemically doped solutions. We observe the existence of two distinct charged excitations in addition to the radical cation. Photoimpedance spectra and some preliminary low temperature spectra provide further insight into these charged excitations.

Keywords: sexthiophene, oligothiophene, photoimpedance, polaron, bipolaron

INTRODUCTION

There has been considerable interest in the study of conjugated oligomers since they can be synthesised with well-defined chain lengths and offer insight into the charge storage and charge transport mechanisms of conjugated polymers, besides being high-performance electronic materials in their own right.

Much of the spectroscopy on charged states of oligomers has focussed on chemical doping studies of dilute solutions in order to approach the limit of isolated systems in which inter-oligomer interactions are negligible[1,2,3,4]. Photo-oxidation studies[5], spectroelectrochemical studies[6] and spectra of charged oligomers formed within the channels of zeolites[7] have also been reported. Most of these techniques yield similar spectral features although a concensus has yet to be reached on the assignments of the electronic transitions.

In view of the potential applications of conjugated oligomers[8,9] and polymers[10,11] in solid-state thin film (opto-)electronic devices, we were motivated to study the nature of the charged excitations of oligothiophenes by opto-electronic spectroscopy of thin film Metal - Insulator - Semiconductor (MIS) devices in which an oligothiophene was the active semiconducting layer.

Because an MIS structure allows purely electrical charging of the oligomeric chains, by the field effect, Voltage - Modulation Spectroscopy[12,13] (VMS) provides a sensitive technique for the study of charged excitations in a solid state device environment, with the effects of inter-oligomer interactions but without the potential steric and coulombic perturbations due to the counter-ions which are present in chemically-doped systems.

Photoimpedance spectroscopy[14,15] (PZS) yields spectral features in correspondence with the optical transitions detected by VMS. PZS also provides additional information which facilitates the interpretation of spectra.

Voltage - Modulation Spectroscopy (VMS) - Principles

The field-induced charge concentration within the MIS device is determined by the voltage applied to the gate electrode. Since α-sexithiophene is a p-type semiconductor, application of a negative gate voltage attracts positive charge carriers to the insulator - oligomer interface to form an accumulation layer. Conversely, a positive gate voltage repels positive charges from the interface and a highly insulating depletion layer forms at the interface.

Superposition of an AC modulation voltage in addition to the DC gate bias results in a temporal modulation of the charge density either within the accumulation layer (for negative DC gate biases) or at the edge of the depletion layer (for positive DC gate biases).

Since charge accommodation is accompanied by a local re-arrangement of bond lengths (lattice relaxation) and the formation of new levels within the semiconductor gap, new optical transitions below the π-π^* absorption can be detected as a weak modulation of the transmission spectrum (up to 1 part in 10^4), appearing at the same frequency as the applied AC modulation voltage.

EXPERIMENTAL

Device Fabrication

For studies in the visible and near infra-red regions, MIS devices were constructed on ITO-coated glass, which had been etched to define two conductive strips, 5mm wide, to act as the ohmic contacts. α-Sexithiophene, (6T), synthesised by one-step coupling of terthiophene[16], was purified by sublimation and thin films (~ 1000Å) were deposited on the substrates by vacuum evaporation. Before evaporating the insulator layer, the substrates were annealled within the evaporator to 200°C for 45 minutes under atmospheric pressure of nitrogen in an attempt to remove remaining solvents or gases and also to try to enhance the alignment of the oligomers by providing thermal energy for re-orientation. After cooling, a thin film (~ 1000Å) of silicon monoxide was vacuum evaporated onto the α-sexithiophene, as the insulator layer. Finally, two semi-transparent gold strips 5mm wide were evaporated as the gate electrodes, in order to fabricate four MIS devices, each of area $(5mm)^2$ where the two pairs of electrodes overlapped at right angles [Figure 1].

Voltage - Modulation Spectroscopy (VMS) - Experimental configuration

The semi-transparent MIS substrate was mounted in a cryostat with optical access and kept under vacuum (3×10^{-6} torr) at ~300K for 24 hours before optical measurements were made. Some preliminary spectra were also taken at lower temperature (~ 170K), using a liquid He continuous flow system.

A 150W tungsten lamp provided white light, which was spectrally resolved using a Spex 1680B double monochromator and filters to block higher order diffracted beams. The monochromatic light was focussed through the cryostat, passing at normal incidence through one device. The transmitted light was then collected by a concave mirror and focussed onto the detector, either a Si photodiode for the visible range (1.2eV - 2.5eV), a Ge detector (0.9eV - 1.5eV) or an InAs detector for the near infra-red range (0.5 - 1.3eV). The signal from the detector was phase-sensitively detected by a Stanford SR530 twin-channel lock-in amplifier. To obtain a transmission spectrum, the lock-in was referenced to the chop frequency of the incident beam. To obtain the modulation spectrum, a sinusoidal AC voltage was applied to the gate electrode of the MIS device and the lock-in amplifier was instead referenced to this voltage modulation frequency. The resulting two-channel (X-Y) data were collected by computer, the normalised modulation spectrum ($\Delta T/T$) was computed and subsequent analysis of correlations between phase response, frequency-dependence and bias-dependence of the spectral features enabled those sharing a common physical origin to be identified.

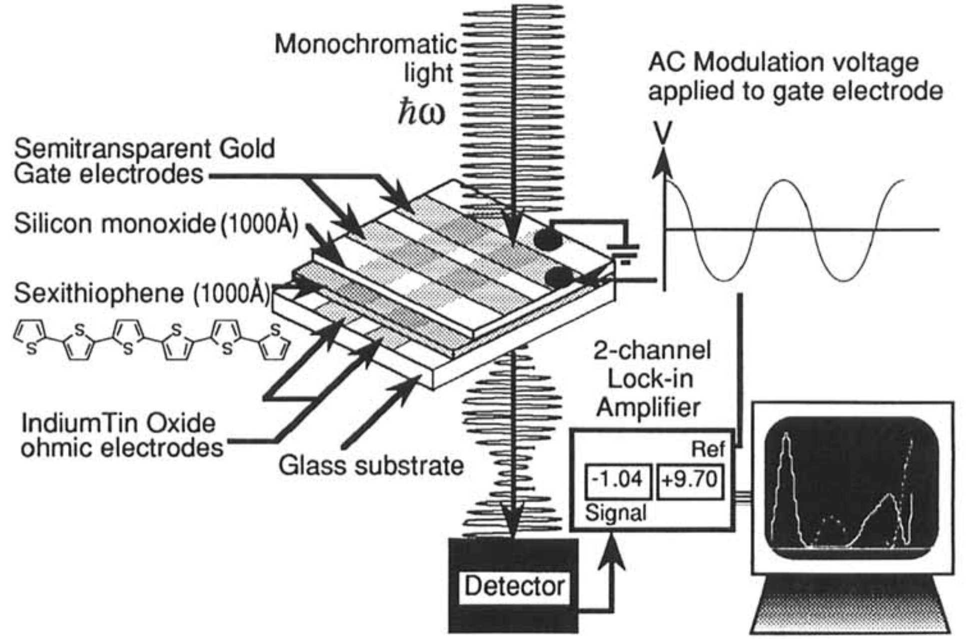

FIGURE 1 Schematic of the experimental configuration for Voltage - Modulation Spectroscopy (VMS).

Photo-impedance spectroscopy (PZS)

Spectrally-resolved photoimpedance (PZS) provides a tool complementary to VMS for detecting deep-lying states within the semiconductor energy gap[14,15]. In contrast with VMS, where an applied electrical signal induces changes in the optical spectrum of the device, photoimpedance spectra show changes in the electrical properties of the device as the energy of the illuminating light is varied. Illumination with light of energy corresponding to the transitions of charged excitations results in a re-distribution of the occupancies of their associated intra-gap levels and the possibility of de-stabilisation of the charged excitation concerned.

Photoimpedance spectra are taken by illuminating the MIS device with monochromatic light and measuring the low frequency impedance (or conductance and capacitance) as the wavelength is varied. Small changes in both real and imaginary components of impedance are detected at wavelengths characteristic of the sub-gap transitions, when the photon energy reaches the threshold for altering the relative populations of deep-lying states within the gap. The same optical configuration is used as for VMS except that instead of applying an electrical signal to the gate electrodes, the low-frequency impedance of the illuminated device is measured by a Hewlett-Packard HP4192A Impedance Analyser. A more intense white light source and slightly wider monochromator slits may be used to increase the intensity of the light which illuminates the device.

RESULTS AND DISCUSSION

Voltage - Modulation Spectra at room temperature

Solid-state thin film spectra [Figure 2] show features in very good agreement with those reported for dilute solutions of α-sexithiophene, chemically doped with $FeCl_3$[1,2,3,4]. Clearly present are the transitions at 0.83eV and 1.70eV, attributed to the radical monocation, $6T^{\bullet +}$. A transition is also observed [Figures 3 & 4] at 1.34eV, whose intensity increases as the charge density within the accumulation layer increases, for increasingly negative DC gate biases. Previously, silicon nitride had been used as an insulator and persistently gave a spurious modulation peak around 1.2eV for many different semiconducting polymers. However, we have verified that silicon monoxide gives no such spurious peaks by taking modulation spectra of a semitransparent SiO capacitor structure. We therefore consider that the 1.34eV feature which we observe is associated with sexithiophene, possibly due to a doubly-charged feature. A transition at 2.05eV is also observed, which is suppressed at higher charge densities [Figures 2 & 4].

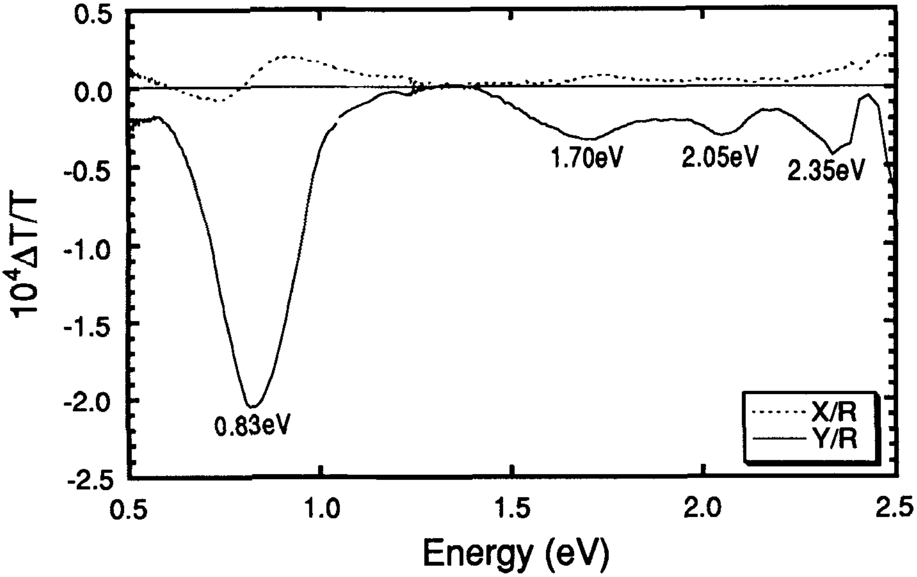

FIGURE 2 Voltage - modulation spectrum of sexithiophene, measured at room temperature, 367Hz modulation, with 0v DC gate bias.

Figure 2 shows the voltage-modulation spectrum obtained at zero DC bias. The in-phase channel (Y/R) shows the modulated absorption features. Both the peaks at 0.83eV and 1.70eV show little change in intensity as the DC gate bias is varied. Their phase and frequency-dependence are also correlated. The correlation between these two transitions is also observed in chemical doping studies, where they are attributed to transitions of the radical monocation. The differential line-shape in the quadrature (X/R) channel, observed for both features suggests that there may be contributions from two distinct sites within the sexithiophene layer, which may have slightly different response times. Given the well-ordered nature of the evaporated thin films, demonstrated by X-ray diffraction[17,18,19], it can be envisaged that such sites may correspond to charged oligomers within the bulk and those at polycrystalline grain boundaries or alternatively, those oligomers lying parallel to the substrate and those showing preferential alignment normal to the substrate.

The feature at 2.05eV does not decrease in intensity even at the highest measurement frequencies, when the DC gate bias is held constant at 0v. However, the feature is almost completely suppressed in accumulation, as shown in Figure 3. Bäuerle[4] and co-workers observe a feature at around 2.0eV in β-didodecylsexithiophene, which they attribute to the transition of a diamagnetic cation π-dimer, $(6T^{\bullet +})_2$. They also observe a blue shift of ca. 0.3eV with respect to the higher energy transition of the monocation (ca 1.5-1.7eV). They only observe a lower energy transition of the π-dimer at lower temperatures.

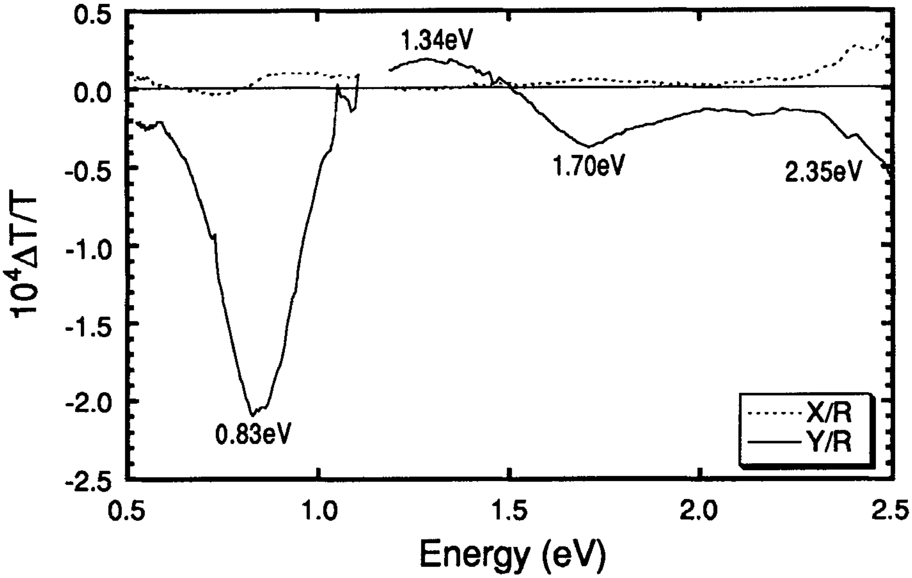

FIGURE 3 Voltage - modulation spectrum of sexithiophene at ~300K, in accumulation, measured at 127Hz, with -4v DC gate bias.

When the device is driven in accumulation (negative gate bias), we observe almost total suppression of the 2.05eV feature at high charge concentrations, and instead, a new feature emerges at 1.34eV, which has its strongest response in full accumulation. The bias-dependence spectra of Figure 4 show this interconversion more clearly. We note that in chemical doping experiments, a transition at around 1.2eV and its shoulder at 1.35eV were observed at high doping levels and attributed to the dication $6T^{2+}$. We believe that the feature we observe at 1.34eV has the same origin. In their studies on charged oligomers within the channels of zeolites[7], Caspar and co-workers observe a much weaker transition at around 2.07eV, which they also assign to the higher energy transition of a dication. Two points should be noted here. Firstly, their spectra are particularly interesting in that they should observe no features due to π-dimers because of the near impossibility of fitting two oligomers within the same zeolite channel, such that they could experience a lateral overlap of their π-electron density. This means that the shoulders they observe should be of a purely vibronic origin. Secondly, because we consider that the relatively strong transition we observe around 2.05eV may be due to π-dimers in the solid state, we would have considerable difficulty in detecting the upper dication transition at a similar energy if it is as weak as that observed by Caspar et al.

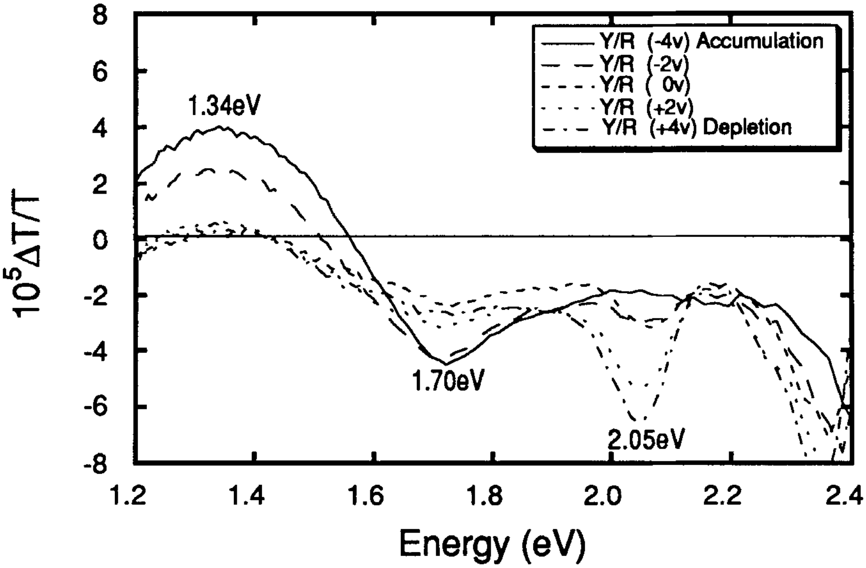

FIGURE 4 DC gate bias dependence of the voltage-modulation spectrum (visible region), measured at 127Hz, at room temperature. Note the emergence of the feature at 1.34eV at high charge densities (accumulation), while the feature at 2.05eV undergoes almost total suppression in accumulation.

Voltage - Modulation Spectra at Low Temperatures

Figure 5 shows the 67Hz voltage modulation spectrum for zero DC gate bias, taken at 170K. Many of the spectral features are still present, though slightly shifted in energy. A new feature appears at 1.01eV, which we consider may be the dimer analogue of the 0.70eV monocation transition, just as the feature at 2.05eV may be a dimer analogue of the 1.70eV monocation transition, with a blue-shift in both cases of around 0.3eV [4]. At high charge concentrations, as probed in accumulation (negative DC gate bias), the dication transition (1.30eV) is again enhanced, while there is appreciable suppression of the monocation transitions (0.70eV and 1.70eV) at low temperatures. This gives further support for our proposed transition assignments and the idea of dication formation from the coalescence of two monocations, this interconversion process being more apparent than at room temperature, where dication formation appears not to reduce the monocation population greatly.

Regarding cation dimers, Bäuerle et al.[4] observed enhancement of the dimer transitions at lower temperatures. In solution, this low temperature enhancement could be attributed to an increase in the dielectric constant of the solvent, leading to increased screening of the cationic charges, reduction of intermolecular repulsion and hence increased stabilisation of cation dimers.

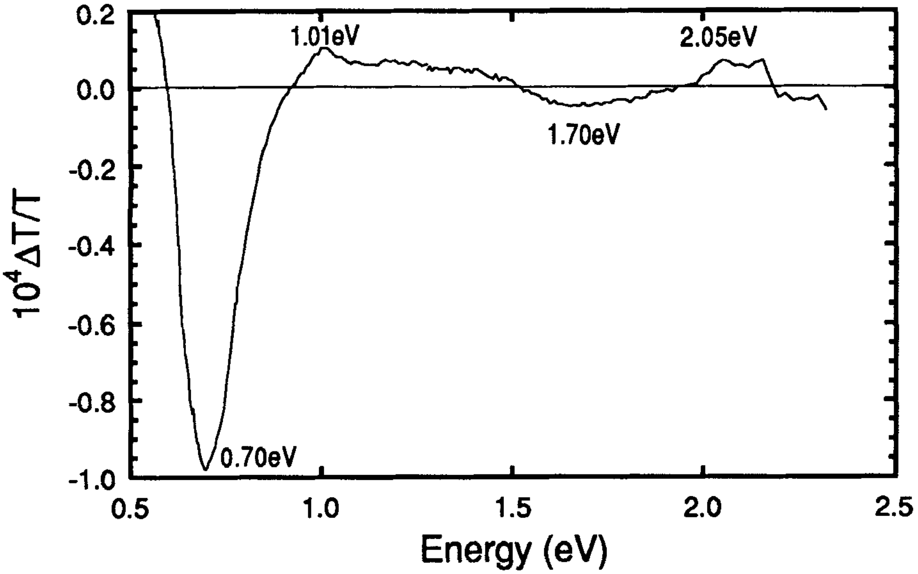

FIGURE 5 Low temperature (170K) Voltage - modulation spectrum of sexithiophene, measured at 67Hz, with 0v DC gate bias.

In solid state films, there should be no solvent molecules to screen the charges, so dimerisation may not be so markedly enhanced at low temperatures, although low temperatures should favour a more ordered structure and a diamagnetic π-dimer or π-stack phase should have a lower spin entropy. Further low temperature spectra are currently in progress.

Photo-impedance spectra

Although still under development, we observe photo-impedance spectra which are qualitatively reproducible. Figure 6 shows the photo-impedance response for a sexithiophene MIS device irradiated with unchopped visible light. Under illumination at certain characteristic wavelengths, both the low frequency device capacitance and conductance change in the same sense, although it is possible that this is due solely to a change in the conductance of the oligomer layer, without any significant change in the depletion layer width.

Both device capacitance and conductance rise sharply when the energy of the illuminating light exceeds 2.05eV. This observation would be consistent with the assignment of the 2.05eV feature to the intra-gap transition of the π-dimer, since such a transition could de-stabilise the dimer, probably resulting in the formation of two radical cations, which may be relatively more mobile.

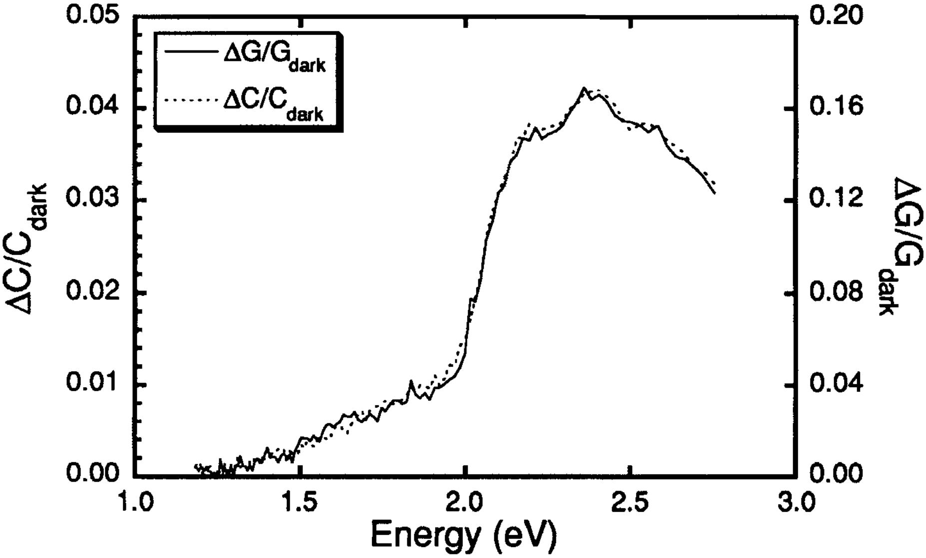

FIGURE 6 Photo-impedance spectrum of sexithiophene, measured at 67Hz, 0v DC gate bias and unchopped illumination.

CONCLUSIONS

The optical spectra associated with charged excitations in solid state thin films of α-sexithiophene are strikingly similar to those of chemically doped dilute solutions. Three distinct charged states co-exist, their equilibrium dynamics determined by the temperature and local charge concentration. We believe these to be the radical monocation, $6T^{\bullet +}$, the diamagnetic cation π-dimer, $(6T^{\bullet +})_2$ and the dication, $6T^{2+}$. It appears that in evaporated solid-state films, the π-dimer is a favourable mode for charge storage at moderately low charge concentrations. At room temperature, sufficient thermal energy exists for a number of mobile radical monocations to be active charge carriers. In addition, at higher charge concentrations, as experienced within the accumulation region of a field-effect transistor, two monocations may coalesce to form a dication and both dications and radical cations can be expected to contribute to the charge transport in field-effect devices.

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