Photoconductivity in poly[[*o*-(trimethylsilyl)phenyl] acetylene]

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Steady-state photoconductivity was studied in thin films of poly[[*o*-(trimethylsilyl)phenyl]acetylene], or poly(*o*-Me_3SiPA) sandwiched between SnO_2 and metal electrodes. Both the dark current density (J_d) and photocurrent density (J_{ph}) depend superlinearly on the applied electric field. J_{ph} also shows a superlinear dependence on light intensity. However, J_d and J_{ph} are only weak functions of temperature at temperatures below room temperature. We conclude that the photoconductivity in poly(*o*-Me_3SiPA) arises mainly from trap-modulated carrier photoemission from electrodes and the polymer is capable of effective transport of holes.

(Keywords: poly[[*o*-(trimethylsilyl)phenyl]acetylene]; photoconductivity; thin film; hole transport)

INTRODUCTION

Electroactive materials derived from conjugated polymers have attracted a great deal of attention in recent years[1]. A survey of the literature reveals that the majority of the studies have been devoted to the dark electrical properties, with somewhat less attention being focused on the optical and photoelectronic properties[2–6]. Since the photoconductive properties of the polymeric materials cannot be readily predicted from the dark conductivity, a continuing need exists for the characterization of polymeric materials having photoconductive properties.

It was found earlier that solution cast films of some polyarylacetylenes, *trans*-polyphenylacetylene (PPA) in particular, are semiconducting photoconductors when undoped; when doped with certain inorganic and organic electron acceptors; and when sensitized with electron-donating dyes[7–9]. In undoped PPA, the majority carriers were found to be electrons, injected from the negatively biased metal electrode through defect states in the band gap of the polymer, with holes being strongly trapped. Optical detrapping was shown to be responsible for the photoconductivity action spectrum that extends well beyond the absorption edge of PPA at about 525 nm and into the near infra-red. Photocurrent to dark current ratio approaching 10^3 could be observed. Thus, it would be of great interest to continue to explore and search for the photoconductive properties in the other derivatives of PPA. This paper deals with the preliminary studies on the photoconductive properties of a Si-containing PPA derivative, poly[[*o*-(trimethylsilyl)phenyl]acetylene] or poly(*o*-Me_3SiPA), synthesized recently in the presence of a transition metal catalyst system[10].

EXPERIMENTAL

Polymer samples

The poly(*o*-Me_3SiPA) sample used in this study was prepared according to the method of Masuda *et al*[10]. The monomer was prepared by methylation at terminal and *ortho* positions of phenylacetylene, followed by silylation at both positions and partial desilylation[11]. Polymerization was carried out in toluene at 30°C in the presence of $WCl_6.Et_3SiH$ catalyst. The polymer so prepared has an average molecular weight in the order of one million. Films for the photoconductivity studies were prepared by casting dilute solutions of poly(*o*-Me_3SiPA) in toluene or chloroform on NESA(SnO_2) or metal-coated glass slides. Residual solvent in the polymer films was removed by pumping under reduced pressure for at least 10 h. The film thickness was determined by weighing. It ranged from 4 to 7 μm and was determined to an accuracy and uniformity of $\pm 10\%$. Metals of various work functions were used for the top electrode. The semi-transparent top electrode with area ranging from 0.05 to 0.2 cm^2 was deposited on top of the polymer film in a vacuum evaporator. A thin lead-in wire was then anchored onto the top electrode by means of conductive silver paste. Thus, the film samples were in a diode-like or sandwich configuration of type metal/polymer/metal or metal/polymer/SnO_2. For comparison photoconductivity in poly(vinyl carbazole) (PVK) and PVK-poly(*o*-Me_3SiPA) composite films were also measured. PVK ($T_g = 200°C$ and $M_w \sim 830000$) was obtained from Aldrich Chemical Co. and was used as received for solution casting into thin films.

Photoconductivity measurements

The continuous light source for this study was provided by a Kratos 150 W xenon arc gas discharge lamp (Model LH 151) with a Kratos LPS 251 power supply. The spectral content and intensity of the light source were controlled by narrow band-pass filters (Oriel Corp.) and various cut-off and neutral-density filters (Ealing Optics). The spectral characteristics and transmittances of these optical filters had been determined spectrophotometrically. A Hewlett-Packard Model 6212B d.c. power supply

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was used for the voltage source, which provided a constant electric field across the polymer film. Dark currents and photocurrents were measured directly with a Keithley Model 614 digital electrometer. All measurements were carried out under atmospheric condition. Radiation was allowed to fall on the transparent SnO_2 electrode in the case of metal/polymer-/SnO_2 structure, and on the semi-transparent top metal contact in the case of metal/polymer/metal structure. Photoconductivity below room temperature was measured *in situ* in a liquid nitrogen cryostat equipped with a quartz window.

RESULTS AND DISCUSSION

Typical dark current–voltage characteristics in Al/Poly(*o*-Me_3SiPA)/SnO_2 and Au/Poly(*o*-Me_3SiPA)/SnO_2 sandwich structures containing polymer film of about 6 μm in thickness are shown in *Figure 1*. The magnitude of the dark current density (J_d) is substantially higher, in the Al/Poly(*o*-Me_3SiPA)/SnO_2 sample, when the SnO_2 contact is at positive bias. Slightly smaller but similar effect of bias on J_d is also observed in the Sn/Poly(*o*-Me_3SiPA)/SnO_2 structure. However, the disparity between positively and negatively biased J_d is reduced significantly when the Al contact is replaced by a high work function metal, such as Au. Furthermore, higher J_d is observed in the case of Au/Poly(*o*-Me_3SiPA)/SnO_2 structure when the Au contact is under positive bias. In all cases, J_d depends approximately on the second power of the applied electric field (E), regardless of the bias on the electrodes. This power law dependence of J_d is indicative of the presence of space-charge-limited current (SCLC), associated with a large population of injected and/or trapped charges[12]. SCLC is also observed in the case of Al/Poly(*o*-Me_3SiPA)/Al cell structure and is included in *Figure 1*. These results clearly show that both the electrode system and the applied electric field will have a significant bearing on the observed dark conductivity of the polymer. The presence of SCLC and the effect of bias have also been widely observed in other photoconductive polymers, such as PPA[6] and PVK[13,14].

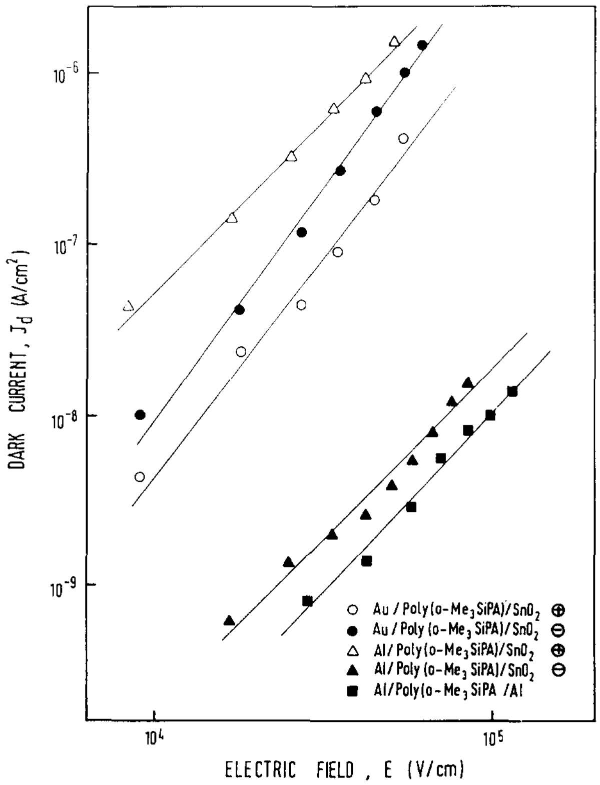

Figure 1 Dark current density as a function of applied electric field in a Poly(*o*-Me_3SiPA) film

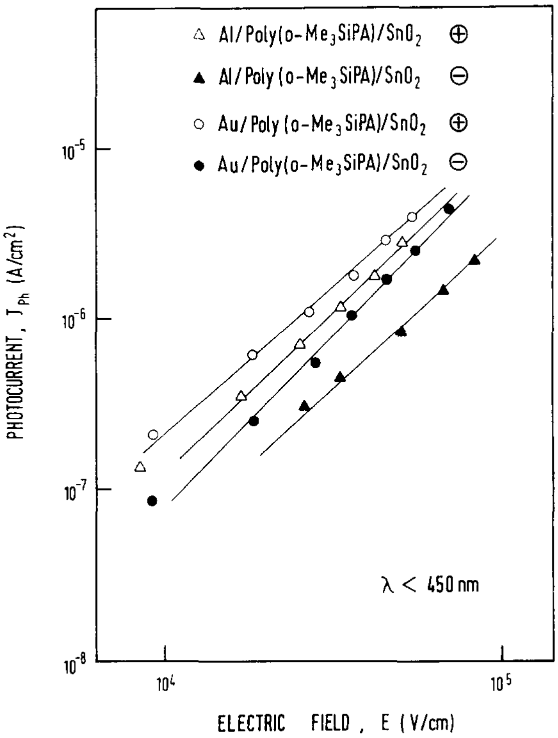

Figure 2 Photocurrent density as a function of applied electric field in a Poly(*o*-Me_3SiPA) film

The effect of bias on the photocurrent (J_{ph}) in the Al/Poly(*o*-Me_3SiPa)/SnO_2 and Au/Poly(*o*-Me_3SiPA)/SnO_2 cell structure is shown in *Figure 2*. In the former, the result is similar to that on the dark current; positive bias on the SnO_2 electrode always generates substantially larger J_{ph}. However, the effect of bias on J_{ph} is substantially smaller than that on J_d. In the case of the Au/Poly(*o*-Me_3SiPA)/SnO_2 structure, the polymer film is sandwiched between two relatively high work function electrodes. J_{ph} is higher when the illumination is through the positively biased electrode. In both samples, a superlinear field dependence of J_{ph} is observed under both bias conditions. Superlinear field dependence of J_{ph} is also observed in samples with Sn and In as top metal contact, as well as when both contacts are Al. The space-charge-perturbed J_{ph} and J_d observed in the present polymer films readily suggest that trap-modulated carrier injection must have occurred at the interfacial region. In the case of the Al/Poly(*o*-Me_3SiPA)/SnO_2 structure, the effect of bias suggests that dark- and photo-emissions are substantially more efficient when the SnO_2 electrode is positively biased. Since Al is a relatively low work function metal we conclude that SnO_2 injects carrier much more readily than Al and that pristine Poly(*o*-Me_3SiPA) is capable of effective transport of holes. This is also supported by the fact that a similar effect of bias on J_d and J_{ph} is observed when PVK film is sandwiched between the SnO_2 and Al electrode. The latter is a well-established hole carrier[13,14]. Furthermore, the photoconductive properties of various Poly(*o*-Me_3SiPA)-PVK composite films, containing substantial and varying amounts of PVK, are not significantly affected by the presence of the latter*. Finally, the magnitude of J_d and J_{ph} and the effect of bias observed in the Au/Poly(*o*-Me_3SiPA)/SnO_2 structure are entirely consistent with the proposed carrier transport process. In this structure, one would expect the threshold for electron emission from either electrode to be quite high.

Photocurrent to dark current ratio approaching 10^3 can be readily observed in the Al/Poly(*o*-Me_3SiPA)/SnO_2 cell when the metal contact is positively biased. However, positive bias on the SnO_2 contact always gives rise to a significantly higher J_d (see *Figure 1*). As a result, the J_{ph}/J_d ratio is substantially reduced under this bias condition, although the magnitude of J_{ph} may be substantially higher than that under the reverse bias condition. The temperature dependence of J_{ph} and J_d in a typical Al/Poly(*o*-Me_3SiPA)/SnO_2 structure is shown in *Figure 3*. J_{ph} is at least two orders of magnitude higher than J_d at the temperature range and electric field specified. The thermal activation energies for both J_d and J_{ph} are relatively small. This relatively weak temperature dependence differs somewhat from that of the PVK films which have activation energies in the range 1–1.5 eV, depending on the work function of the metal electrode used[13]. Nevertheless, this weak temperature dependence, together with the presence of SCLC, are probably consistent with the carriers injection and the presence of shallow monoenergetic traps[15].

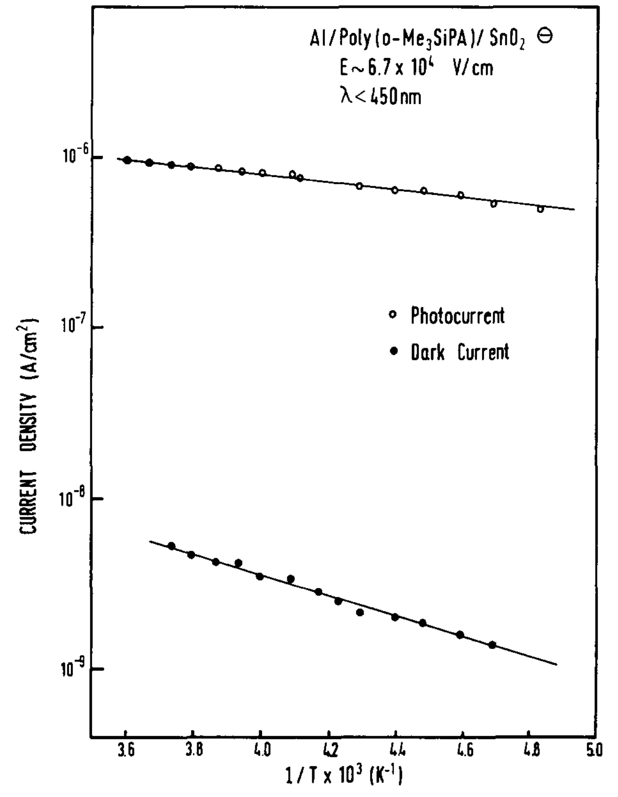

Figure 3 Temperature dependence of the dark current and photocurrent ($E \sim 6.7 \times 10^4\ V\ cm^{-1}$, $\lambda < 450$ nm)

The light intensity (*I*) dependence of J_{ph} in a typical Al/Poly(*o*-Me_3SiPA)/SnO_2 structure is shown in *Figure 4*. The slope of the log–log plot is substantially greater than 1. The superlinear dependence on *I* is also observed when both contacts are Al, as well as in samples with Au, Sn or In as top metal contact. The superlinear intensity dependence is somewhat surprising since most of the changes that one would expect to occur at high light intensities would tend to lead to sublinearity. However, superlinearity may also arise from the sensitization by electronic doping[16], in which the higher light intensity may have caused the steady-state Fermi levels to move sufficiently apart towards the energy band edges.

The spectral response of Poly(*o*-Me_3SiPA) is somewhat interesting and depends on the nature and bias of the electrodes. The polymer film is dark purple in colour and shows a very broad absorption peak centred at about 570 nm[10]. For illumination through the negatively biased SnO_2 electrode in a typical Al/Poly(*o*-Me_3SiPA)/SnO_2 structure, practically no photocurrent was observed for light source with wavelength (λ) greater than 450 nm. On the other hand, however, if the SnO_2 electrode is positively biased, substantial photocurrent can be observed in the red region. However, the photocurrent action spectrum corresponds only roughly to the polymer absorption spectrum and extends somewhat beyond the absorption edge of the polymer, as shown in *Figure 5*. Furthermore, for polymer film sandwiched between two identical low work function Al

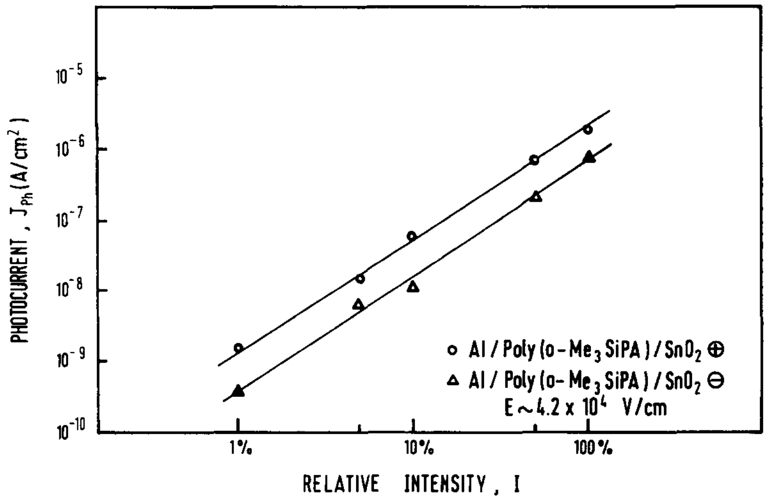

Figure 4 Photocurrent density vs. light intensity in Poly(*o*-Me_3SiPA) film

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* Poly(*o*-Me_3SiPA)–PVK composite films remain relatively uniform and homogeneous even at PVK content as high as 20 mol%

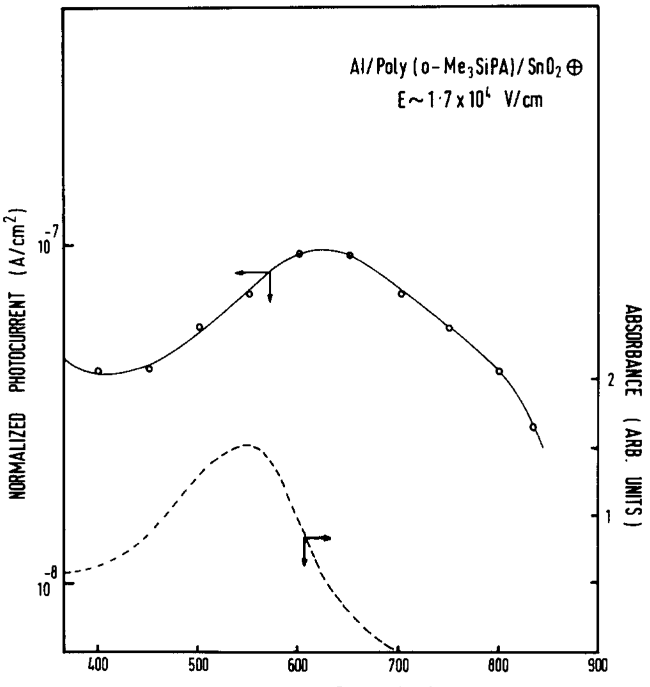

Figure 5 Photoconductivity action spectrum and absorbance

electrodes, large J_{ph}/J_d ratios are observed only when illumination is through the positively biased electrode with light source in the near-ultra-violet region. Thus, the lack of exact correspondence between J_{ph} and absorption spectrum, the effect of bias on the illuminated electrode and the presence of J_{ph} beyond the absorption edge of the polymer in some cases are all consistent with the proposed carrier injection process and the presence of a trap-modulated J_{ph}.

CONCLUSIONS

Good photoconductive properties were observed in thin films of Poly(*o*-Me_3SiPA) sandwiched between SnO_2 and metal electrodes. Both the dark current and photocurrent depend strongly on the type of electrode and the bias condition. The observed photoconductivity appears to be consistent with a trap-modulated carrier photoemission process at the polymer–electrode interface.

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