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Carrier Generation Processes in Poly(*N*-Vinylcarbazole) Films

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Studies on the conductivity and photoconductivity of amorphous films of poly (*N*-vinylcarbazole) with SnO_2 and metal electrodes show that the dark conductivity is dominated by the Richardson-Schottky field-assisted hole emission from positively biased metal electrodes, provided the metal work function is greater than 3.8 eV. When the metal electrode is negatively biased or with lower-work-function electrodes, the conductivity appears to be dominated by a bulk-polymer-film effect. The current-voltage characteristics of the latter effect do not support a Poole-Frenkel process. High-work-function metal electrodes in positive bias give rise to hole-photoemission tails in the photocurrent-action spectrum. A photocarrier generation process, which onsets at 1.8–1.9 eV and obscures hole photoemission from low-work-function metal electrodes, produces a linear dependence of photocurrent on light intensity and appears to be associated with electronic transitions in the polymer film.

INTRODUCTION

A considerable amount of progress has been made in understanding photoconductivity and semiconductivity phenomena in organic crystals in recent years.[1] The situation with regard to understanding similar phenomena observed in organic polymers is less satisfactory. This can be largely attributed to the greater difficulties in obtaining well-characterized samples and the semi- or noncrystalline nature of polymer specimens. The increasing importance of polymeric materials in electrophotography and recent emphasis on the electronic properties of amorphous materials in general has, however, stimulated a renewal of interest in both carrier generation and transport in polymers. Carrier mobilities have been reported in poly (*N*-vinylcarbazole)[2] (PVK), polyvinylchloride,[3] and other polymers.[4] Photoinjection of carriers through electrodes[5] and photocarrier generation via excitons[6] have also been investigated. Progress has been made in understanding mechanisms of spectral sensitization in poly(*N*-vinylcarbazole).[7]

Recent studies on photoinjected space-charge-perturbed currents in PVK films are particularly intriguing because they indicate that deep carrier trapping may not be a major problem in relatively uncharacterized amorphous materials in contrast to the situation that obtains in the case of organic molecular single crystals.[2(e)] These findings, in conjunction with hole-photoemission studies on metal-PVK-SnO_2 samples,[5(a)] indicate that the dark-conduction mechanism is likely to be dominated by the Richardson-Schottky field-assisted thermionic hole emission. To determine the extent to which this mechanism is operative and also gain additional information on photocarrier generation in amorphous PVK, steady-state-photoconductivity and dark-conductivity measurements have been carried out on metal-PVK-SnO_2 samples with metals having work functions in the range 3.8–6.3 eV.

EXPERIMENTAL TECHNIQUES

Optically clear PVK films were cast evenly on the conducting side of ultrasonically clean Nesa glass from a solution consisting of 17% PVK, 17% cyclohexanone, and 66% toluene by weight. The sample was placed in a saturated atmosphere of the solvent 1 : 4 (cyclohexanone-toluene) for 4–5 h then dried at (65–70) °C, for 4–8 h. A metal film (thickness 800 Å; area 5–6 cm^2) was vacuum evaporated onto the PVK to complete the electrode system. The PVK film thicknesses were determined by capacitance measurements to be $30 \pm 5\ \mu$.

The experimental arrangement used for the pho-

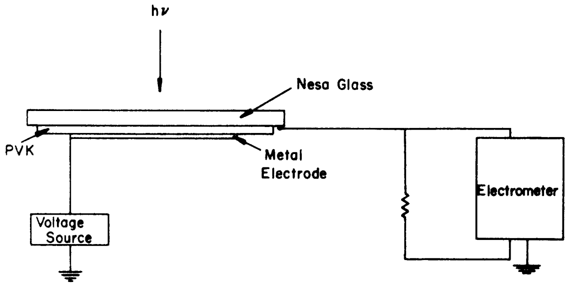

FIG. 1. Experimental arrangement.

toemission photocurrent is shown in Fig. 1. Monochromatic light was obtained from a Bausch-Lomb 33-86-25-02 monochromator and xenon light source, equipped with appropriate filters to remove higher-order wavelengths. The monochromator-light-source arrangement delivered approximately constant photon flux at the sample over the photon energy range 1.5–3.0 eV. Steady-state photocurrents were measured with a Cary-401 vibrating-reed electrometer in conjunction with a Varian G-2000 recorder. A Keithley-241 regulated high-voltage supply supplied the voltage bias at the metal electrode.

The same arrangement was used to measure steady-state dark currents over the voltage range 10–500 V. Samples yielding dark currents in excess of 10^{-10} A at 80 V, were considered unsatisfactory and were not investigated further.

RESULTS AND DISCUSSION

Photoemission Studies

With high-work-function metal electrodes it was generally found that photocurrent tails in the action spectrum extended to lower photon energies when the metal was biased at positive voltage. A common photocurrent threshold (at ~ 1.8–1.9 eV) was observed when the metal electrodes were biased negative and also for samples equipped with two Nesa glass electrodes. This was considered to be the onset of photocarrier-generation processes involving electronic transitions in the polymer film.[2(a),(b)] The photocurrent tails extending to lower photon energies were attributed to hole photoemission since plots of the square root of the quantum yield ($Q^{1/2}$) versus photon energy were linear from the measurable onset of the photoemission current to photon energies greater than 1.7–1.8 eV.

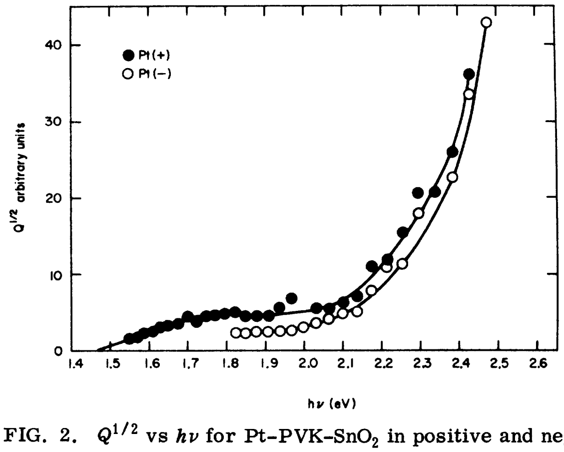

FIG. 2. $Q^{1/2}$ vs $h\nu$ for Pt-PVK-SnO_2 in positive and negative bias.

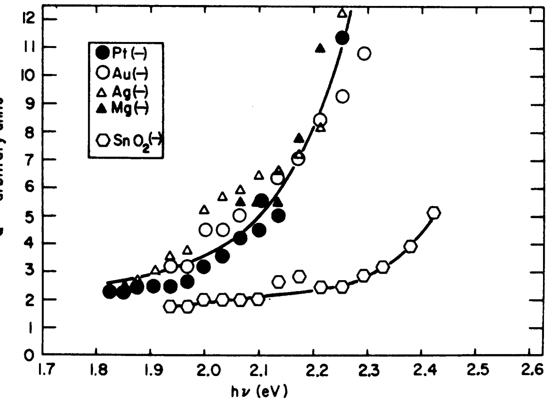

FIG. 3. $Q^{1/2}$ vs $h\nu$ for several metals in negative bias.

Figure 2 shows typical photocurrent spectra obtained for a platinum electrode, with the applied voltage at ± 80 V. Photocurrent spectra for several electrode systems with the metal at negative bias and also for an all SnO_2 electrode system are shown in Fig. 3. Plots of $Q^{1/2}$ versus photon energy for several metal electrodes at positive bias in the photoemission region are shown in Fig. 4. These plots were used to determine photoemission thresholds, extrapolating to zero quantum yield and assuming the Fowler relationship[8]

$$Q \sim (\Phi - \Phi_h)^2, \qquad (1)$$

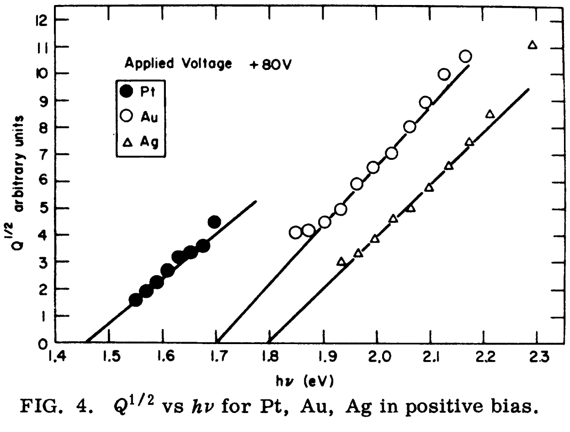

FIG. 4. $Q^{1/2}$ vs $h\nu$ for Pt, Au, Ag in positive bias.

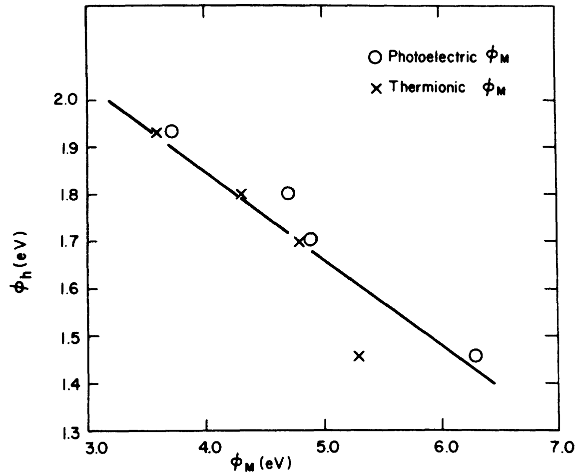

FIG. 5. Hole-photoemission threshold Φ_h vs metal work function Φ_M.

where Q is the quantum yield, in arbitrary units, Φ is the photon energy of radiation ($h\nu$), and Φ_h is the hole-photoemission threshold. This relationship is considered a good approximation for $\Phi - \Phi_h > 3kT$.

Photoemission thresholds determined in this way for Pt, Au, Ag, and Mg are plotted against metal work function[9] Φ_M in Fig. 5. A general trend to lower the photoemission threshold was found as Φ_M increased. An estimated threshold for the magnesium electrode is included which fits the general trend. The positive-bias photocurrent data in the case of magnesium were, however, virtually identical to the negative-bias data shown in Fig. 3. This indicates that hole-photoemission tails in the photocurrent spectrum cannot be readily separated from other photocarrier generation processes if Φ_M is less than 3.65–3.8 eV. Lower-work-function metal electrodes than this would have to be employed in order to produce electron photoemission tails. Extrapolation of the cube root of the quantum yield against $h\nu$ yielded slightly lower photoemission thresholds.[10] The trend illustrated in Fig. 5 was still apparent, however. Hole-photoemission thresholds are summarized in Table I along with values of $\Phi_h + \Phi_M$. The latter quantity represents an estimate of the valence-band-edge position in PVK relative to the vacuum level. The average value is 6.4 eV, in good agreement with previously reported experimental values and theoretical estimate.[5(a)]

The photocurrents obtained at photon energies greater than 1.8–1.9 eV were much higher in magnitude and the dependence of photocurrent on radiation intensity was measured. The results are shown in Fig. 6. In general an approximately linear relationship was obtained indicating that the photocarrier generation process onsetting at 1.8–1.9 eV is most likely an exciton process involving possibly the dissociation of singlet excitons at a surface impurity or defect site. Such mechanisms are known to be operative in organic molecular crystals in spectral regions where excitons can be produced.[1] There was no evidence for the exciton-exciton annihilation mechanism often found in molecular crystals.[11]

TABLE I. Summary of hole-photoemission thresholds and work-function data. Φ_{MP} is the photoelectric metal work function and Φ_{MT} is the thermionic metal work function. All units expressed in eV.

Metal	Φ_{MP}[a]	Φ_{MT}[b]	Φ_h	$\Phi_{MP}+\Phi_h$	$\Phi_{MT}+\Phi_h$
Pt	6.3	5.3	1.4	7.7	6.7
Au	4.9	4.8	1.7	6.6	6.5
Ag	4.7	4.3	1.8	6.5	6.1
Mg	3.7	3.6	1.9	5.6	5.5

[a] Reference 9(b).
[b] Reference 9(a).

Dark-Current Studies

Steady-state dark-current (J)–voltage (V) characteristics were obtained with the metal electrode biased both positive and negative, in order to determine the extent to which Richardson-Schottky field-assisted thermionic hole emission contributes to the conductivity.

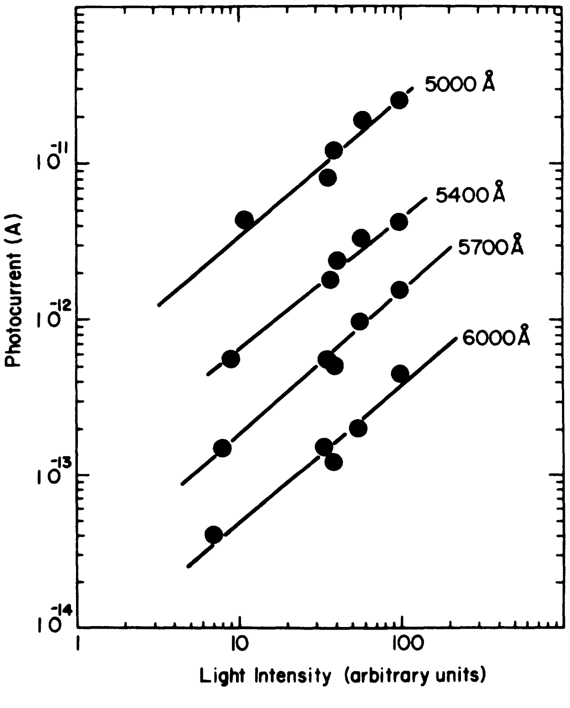

FIG. 6. Photocurrent vs light intensity.

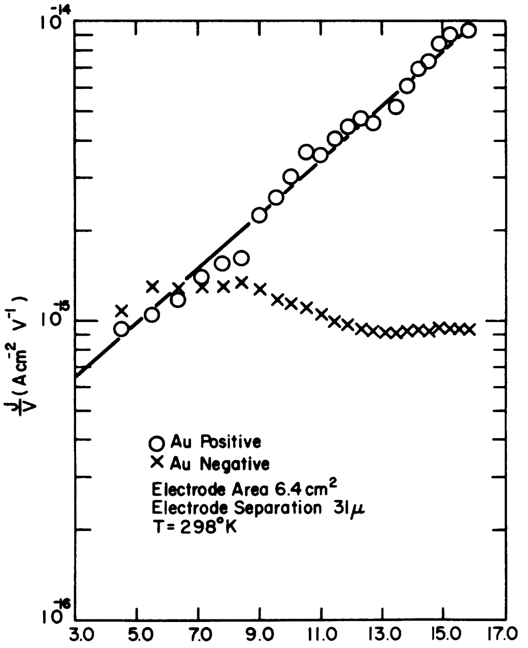

FIG. 7. $\ln(J/V)$ vs $V^{1/2}$ for Au-PVK-SnO$_2$.

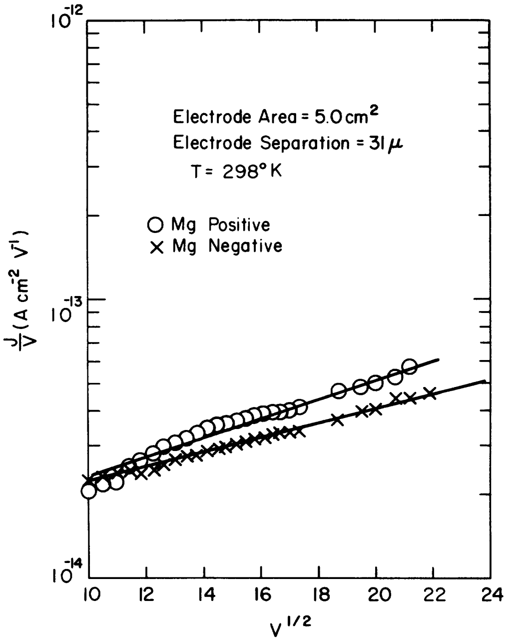

FIG. 8. $\ln(J/V)$ vs $V^{1/2}$ for Mg-PVK-SnO$_2$.

Previous studies have shown that three conductivity mechanisms must be considered.[12] The classical Richardson-Schottky effect predicts a current-voltage characteristic of the form

$$J = AT^2 e^{-\Phi_S/kT} e^{\beta_S V^{1/2}}, \tag{2}$$

with

$$\beta_S = \frac{e}{kT}\left(\frac{e}{4\pi\epsilon\epsilon_0 d}\right)^{1/2}, \tag{3}$$

where J is the current density, A is a constant, T is the absolute temperature, e is the electronic charge, V is the voltage, Φ_S is the (Schottky) electrode barrier, k is Boltzmann's constant, d is the film thickness, ϵ is the dielectric constant, and ϵ_0 is the permittivity of free space. Equation (2) thus predicts a linear relationship between $\ln J$ and $V^{1/2}$ of slope β_S at constant temperature. In the case of low-mobility materials,[2] the diffusion-limited Richardson-Schottky equation must be considered.[13] This predicts a linear relationship between $\ln(J/V)$ and $V^{1/2}$ of slope β_S. If the Poole-Frenkel effect is operative a linear relationship between $\ln(J/V)$ is again predicted but the slope can be β_S or $2\beta_S$.[14] Nonlinear $\ln J - V^{1/2}$ plots were generally obtained for the metal electrode biased both positive and negative. Figure 7 shows a typical $\ln(J/V) - V^{1/2}$ plot. Plots of this type were found for samples equipped with Au, Pt, and Ag electrodes. Experimental β_S values obtained from the linear positive-bias data were in good agreement with theoretical β_S values calculated from Eq. (3), using $d = 30$ μ and $\epsilon = 3.75$.[2(a)] $\ln(J/V)$ was almost constant with $V^{1/2}$ when the metal was at negative bias yielding zero or very small experimental β values. A similar plot obtained with a magnesium electrode is shown in Fig. 8. In this case the positive-bias data were similar to the negative-bias data, both plots yielding experimental β_S values smaller than the theoretical value. Experimental β values are summarized in Table II. The results generally indicate that diffusion-limited Richardson-Schottky hole emission is the conduction mechanism with Au, Pt, and Ag electrodes biased positive. With these electrodes biased negative the barrier for electron emission is high and another carrier generation mechanism controls the dark current. This may be a process involving the SnO$_2$ electrode

TABLE II. Comparison of experimental and theoretical β values.

Metal	$\beta_{\text{Expt}}(V^{-1/2})$ metal positive	$\beta_{\text{Expt}}(V^{-1/2})$ metal negative
Pt	0.18	...
Au	0.22	...
Ag	0.17	0.02
Mg	0.09	0.06
Theoretical		
	$\beta_{PF}(V^{-1/2})$	$\beta_S(V^{-1/2})$
	0.27	0.14

or a bulk phenomenon in the polymer film. However, the current-voltage characteristics do not support a Poole-Frenkel process. When the metal work function is reduced further, i.e., Mg, the barrier to hole emission is high and the conductivity characteristics in both positive and negative bias are similar indicating that the same process is dominating. The similarity of the negative- and positive-bias characteristics indicates that a bulk carrier generation phenomenon dominates. The characteristics do not support a Poole-Frenkel mechanism. The electron emission barrier is still not low enough for the Richardson-Schottky electron emission to dominate.

CONCLUSIONS

Photoconductivity studies have shown that part of the photocurrent action spectrum in poly(*N*-vinylcarbazole) films is due to hole photoemission from positively biased metal electrodes provided the metal work function is greater than ~ 3.8 eV. Hole photoemission is not readily observed if the metal work function is less than this due to the onset of another photocarrier generation process at 1.8–1.9 eV, which appears to be a characteristic of the polymer film. A work function of 3.8 eV is not low enough to produce electron photoemission beyond the long-wavelength edge of the process which onsets at 1.8–1.9 eV. This is consistent with the band structure of PVK suggested previously.[15] The photocarrier generation process which onsets at 1.8–1.9 eV yields a linear dependence of photocurrent on light intensity. This process, which appears to involve electronic excitations in the polymer, is most likely due to exciton dissociation at electrode, impurity, or defect sites[1] or an interaction of excitons with trapped carriers.[6]

Dark-conductivity studies strongly indicate that the dominant dark-conductivity mechanism is diffusion-limited Richardson-Schottky hole emission when metal electrodes having work functions greater than 3.8 eV are employed in positive voltage bias. In metal-PVK-SnO_2 systems, with the metal at negative bias, the dark conductivity is controlled by another process, whose current-voltage characteristics do not fit either Richardson-Schottky or Poole-Frenkel mechanisms. With a magnesium electrode ($\Phi_M \sim 3.8$ eV) the same process is found with both positive and negative metal-electrode bias, indicating possibly a bulk effect in the polymer. The metal work function is not low enough for Richardson-Schottky electron emission to be a dominant factor. Conduction-activation-energy magnitudes obtained from dark-current–temperature studies tend to support the above conclusions.[11] A well-defined dependence of activation energy on metal electrode was not, however, observed.

ACKNOWLEDGMENTS

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