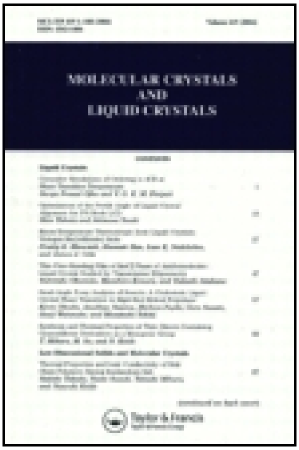

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Current-Voltage Characteristics of Carbazole Modified Polysiloxanes

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CURRENT-VOLTAGE CHARACTERISTICS OF CARBAZOLE MODIFIED POLYSILOXANES.

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ABSTRACT. Current-Voltage characteristics are presented for Metal/CMPs/Metal structures. An apparently ohmic behaviour is observed at low fields, while superlinear behaviour is observed at higher fields for high work function metals. The temperature dependence of the inferred conductivity in the low field region is similar to that of the carrier mobility determined from transient measurements. The high field current-voltage relationship is associated with a breakdown mechanism.

INTRODUCTION

Carbazole modified polysiloxanes (CMPs) are of interest due to potential applications in electro-optic systems. Their specific benefits[1] derive from the range of synthetic routes whereby the carbazole moiety may be attached to the flexible siloxane backbone. Previous work[2,3] on CMPs has focussed on the measurement of excess-carrier mobility and its dependence on electric field and temperature. In this paper we focus on the dark current-voltage characteristics.

EXPERIMENTAL DETAILS.

CMPs (figure 1) were prepared via platinum catalysed hydrosilylation reactions between polymethylhydrosiloxane (Petrarch, molecular weight = 2250 (n=35)) and carbazol-9-ylalk-1-enes, as previously reported[1,4]. Thin films were spun onto prepatterned metallised glass substrates from 0.015-0.03 M solutions of CMPs (m = 3) in chloroform at speeds of 700-4000 RPM giving films of thickness 6 - 1 μm. To obtain reproducible data, films had to be vacuum dried at ≈ 45°C for ≈ 6 hours.

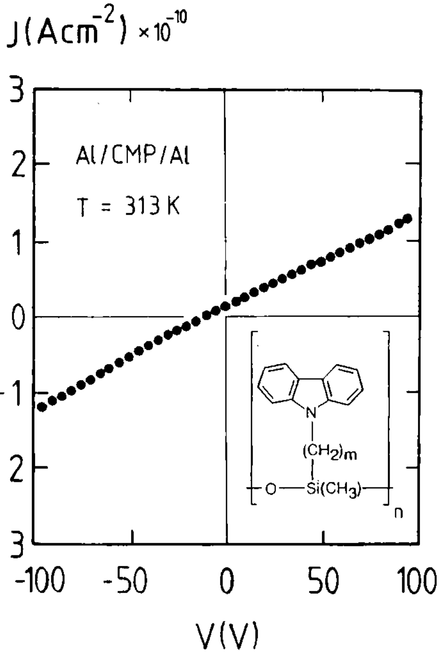

FIGURE 1 J-V Plot for a symmetric Al/CMPs/Al structure. Film thickness 2.5μm. Inset: Chemical structure of CMPs.

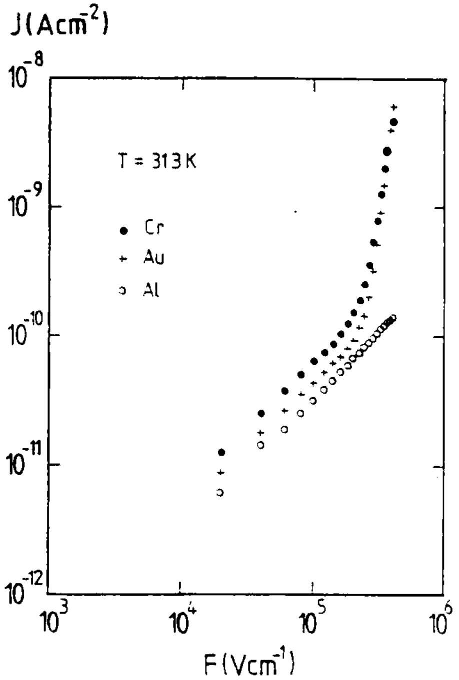

FIGURE 2 Double logarithmic plot of J vs F for Al/CMPs/Al, Al/CMPs/Cr and Al/CMPs/Au structures at 313K. Top Al negative in all cases.

Electrical contacts (M1) on the glass substrate were provided by sputtered metals with work functions in the range 3.8 - 5.1 eV, while the top contact (M2) was always fabricated from aluminium (Al). (This minimised film damage due to sputtering of the polymeric layer.) The active device area was 0.04 cm^2.

Electrical measurements were performed under computer control in an evacuated environmental chamber using a Keithley 617 electrometer. The limit of current resolution was $\approx 10^{-13}$ A which restricted the experimentally accessible range of electric field F and temperature T to be greater than 10^4 V cm^{-1} and 280 K, respectively. For even higher electric fields and temperatures electromechanical breakdown was observed as T approached T_g (330K for m = 3) and F exceeded 1 MV cm^{-1}. At each electric field the samples were allowed to stabilise for 300s and the current was taken as an average of several readings over further 30s intervals.

RESULTS AND DISCUSSION

Current density-voltage (J-V) characteristics for a symmetric Al/CMPs/Al structure are shown in figure 1. The symmetric nature of the characteristic is to be noted, indicating that the contacts formed when the polymer is spun onto the metal is not different in nature from that formed when the metal is deposited on the polymer.

J-F characteristics for a range of samples with different substrate metallisations M1 are shown in figure 2. For low work function (W) metals, (Magnesium (Mg), W = 3.8 eV; Al, W = 4.2 eV), an apparently ohmic behaviour is observed over the experimentally accessible range of electric field. However, for higher work function metals, (Chromium (Cr), W = 4.6 eV; Gold (Au), W = 5.1 eV), an apparently ohmic region is observed only at lower fields with a superlinear behaviour of the form $J \alpha V^n$ ($n \approx 5 - 10$).

Studies of drift mobility in carbazole-containing polymers[5] have suggested that the current is carried by holes due to the relative ease of electron transfer from neutral molecules to adjacent cation radicals compared to the difficult formation of the anion radicals. However, these transport active states are thought to be $\approx$ 1-2 eV[5] above the Fermi levels of the metallic contacts employed in this study, and therefore the contacts should be emission limiting or blocking. Therefore, given the low mobilities reported for CMPs, the dc electrical characteristics would be expected to conform to the diffusion-limited Richardson-Schottky formalism[6] with $J/V \alpha F^{1/2}$. The dc electrical currents observed in many carbazole-containing polymers are found to be significantly higher than predicted for an ideal contact. Various explanations[7] have been proposed which incorporate the influence of surface states and tunnelling processes to mediate charge transfer between metal and polymer. However, the existence of 'ohmic' regions may only be explained by postulating the complete absence of barrier effects.

Assuming that barriers to carrier injection do not exist, one can determine the temperature dependence of the material conductivity σ in the 'ohmic' region as shown in the Arrhenius plot of figure 3. Data have been obtained for two samples with metals of different work functions (3.8 eV and 5.1eV). It is seen that the conductivities of both specimens are similar in magnitude and that a well defined activation energy E_σ of 0.72eV is obtained. This provides further support for the idea that the currents are due to the bulk generation of carriers within the polymer layer. The conductivity of a material (assuming only one carrier type) depends upon the number density of the charge carriers and their associated mobilities. Studies[3] of the transport of photogenerated holes in Al/CMPs/Al structures (at high electric fields) reveal that the log of the carrier

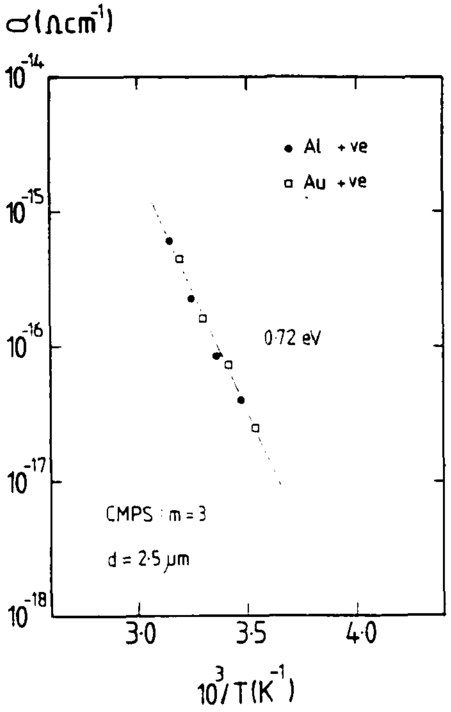

FIGURE 3 Logarithm of σ vs 1/T for Al/CMPs/Al and Al/CMPs/Au structures. Top Al -ve in all cases.

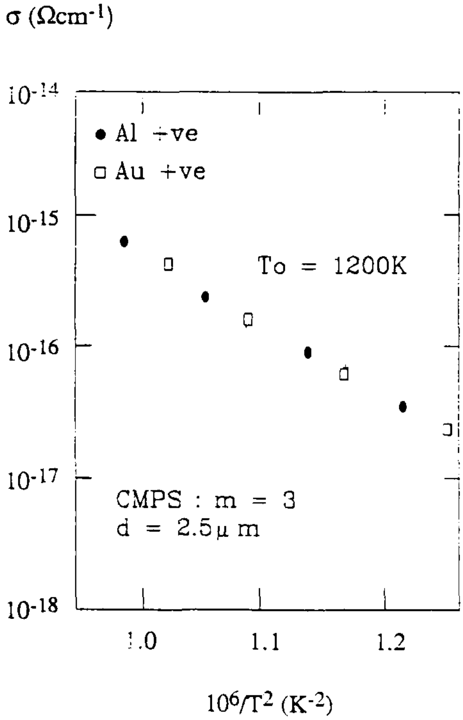

FIGURE 4 Logarithm of σ vs $1/T^2$ for Al/CMPs/Al and Al/CMPs/Au structures. Top Al negative in all cases.

mobility varies as the square root of the electric field. This should be reflected in the bulk conductivity, but is not observed here. However, recent experimental work[8] on other disordered polymers suggests that this field dependence becomes significantly weaker at lower electric fields. Since these J-V measurements have been performed at lower electric fields, the apparent absence of field-enhanced conduction may be understandable.

E_σ should consist[9] of a component due to the thermal generation of charge carriers and one due to the hopping activation energy (assuming the charge transport process involves thermally activated steps). The two analytical procedures[8,10] currently used to explain the temperature dependence of the carrier mobility approach the problem from different viewpoints. The trap limited procedure[10] assumes that the mobility is rate limited by interactions with deep traps. Application of this procedure[3] for CMPs yields a mobility activation energy of ≈ 0.8 eV, very close in value to the conductivity activation

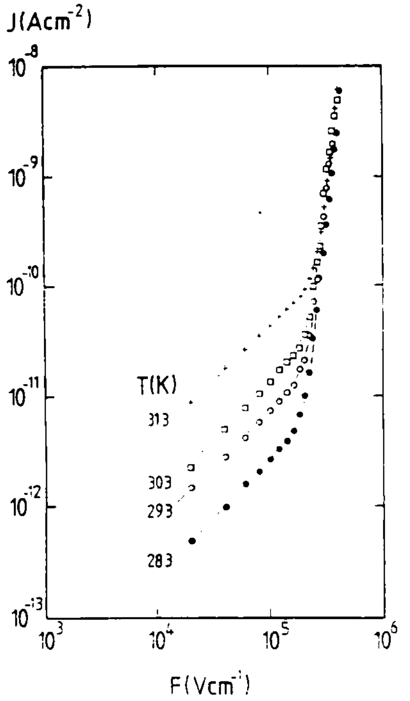

FIGURE 5 Double logarithmic plot of J vs F parametric in T for an Al/CMPs/Au structure. Al negative.

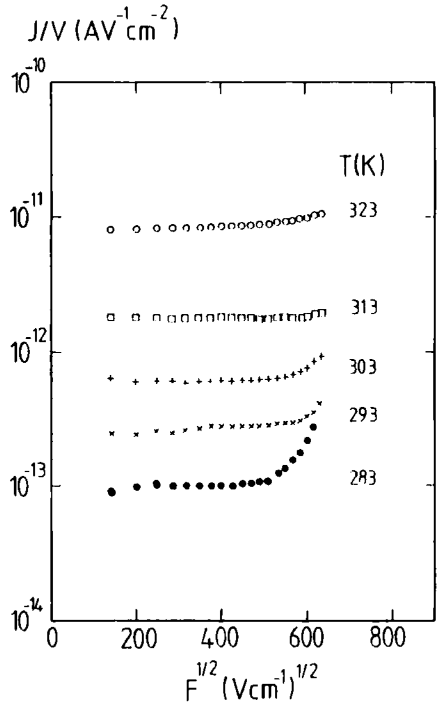

FIGURE 6 Logarithm (J/V) vs $F^{1/2}$ for an Al/CMPs/Au structure, parametric in T. Al negative in all cases

energy. Given that the energetic difference between HOMO and LUMO states for the carbazole molecule is several eV[5], it can only be postulated that charge must be generated through extrinsic centres situated close in energy to the transport active state. The trap free model[8] envisages charge transport as occurring via a hopping process through a gaussian distribution of localised centres. Analysing mobility data for CMPs in this fashion[3] suggests that the gaussian half-width of the distribution is $\approx$ 0.15 eV. Assuming that the conductivity temperature dependence arises solely from that of the mobility, the logarithm of the conductivity should be a function of $1/T^2$ (figure 4), with the slope yielding the characteristic temperature T_0 of the assumed gaussian distribution. Application of this procedure leads to a Gaussian half width of 0.155 eV (= $1.5kT_0$), in line with that obtained from mobility measurements[3]. Again, it must be postulated that the carriers originate from extrinsic centres. From the measured electrical conductivities and mobilities the density of these extrinsic centres can be estimated to be $\approx 10^{10}$ cm^{-3}.

The onset of the superlinear regime appears to occur at around 0.15 MV cm^{-1} (figures 2 and 5) approximately independent of temperature, but dependent on metal work function. Figure 6 shows that the breakdown process is progressively swamped at higher temperatures by the bulk generation of carriers. Due to the absence of superlinear behaviour in specimens contacted with low work function metals, it is possible to rule out field-enhanced conduction as the mechanism responsible. Mobility measurements[2,3] show that at higher electric fields, the logarithm of the mobility depends upon $F^{1/2}$ and not upon F^n where $n \approx 5\text{-}10$ as required to explain the superlinear behaviour of the conduction process. Therefore, it is believed that a breakdown process is occurring above a critical field (dependent on W). This process is found to be completely reversible. The origin of this breakdown process and its dependence upon metal work function are matters still to be resolved. Further experimental studies are underway to address these issues.

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