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Effect of Gases on the Conductivity of Organic Solids. IV. Site of Carrier Injection

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Abstract—Evidence suggesting the involvement of the electrode–crystal interface in ambient vapor induced charge carrier injection phenomena in organic crystals is presented. Space-charge-limited currents are not observed until high voltages are applied when superlinear current–voltage characteristics indicating such effects are also found in the unexposed crystal. Drift mobility measurements on anthracene crystals exposed to iodine vapor confirm that the ambient vapor induced bulk conductivity effects are phenomena involving the production of charge carriers.

Introduction

Previous publications in this series[1–3] have demonstrated that bulk conductivity increases may be observed in electron acceptor and donor crystals on exposure to vapors with electron donor and acceptor properties respectively. *p*-Chloranil crystals exposed to ammonia and amine vapors and anthracene crystals exposed to iodine vapor were the systems studied. The phenomena observed were attributed to charge carrier injection induced by donor–acceptor interaction at the crystal surface, rather than an effect on charge carrier mobility. Evidence is now presented that such ambient vapor induced carrier injection processes most probably take place at the electrode–crystal interface. Measurements of carrier drift mobility in anthracene crystals in the presence of ambient vapor confirm that the induced bulk conductivity effects are phenomena involving solely the production of charge carriers.

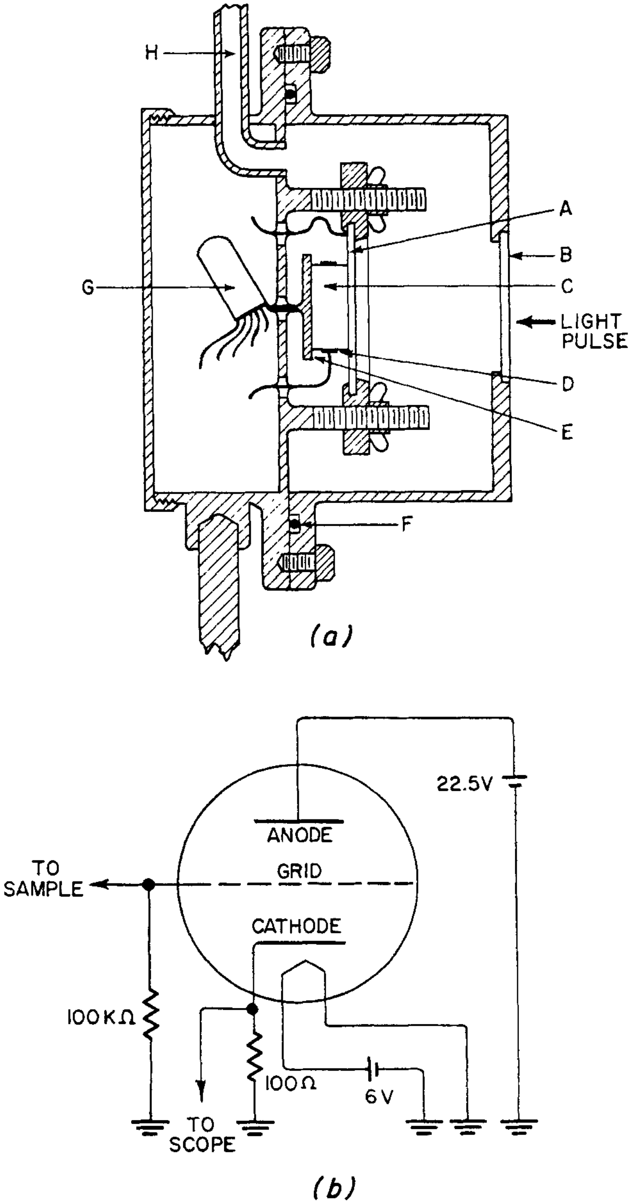

Figure 1. General arrangement for transient photoconductivity measurements. (a) Drift mobility cell: A, semitransparent electrode (high impedance); B, quartz window; C, crystal sample; D, grounded guard ring; E, low impedance electrode; F, vacuum O-ring; G, nuvistor-8056 RCA; H, vacuum vent. (b) Cathode follower circuit (nuvistor-8056 RCA).

Experimental

Steady state conductivity measurements were carried out utilizing the techniques described previously.[1,2] The apparatus used to investigate photocurrent transients produced by pulsed light is shown in Fig. 1, the method of measurement being similar to that described by Kepler.[4] All metal parts inside the vacuum chamber were gold plated in order to avoid iodine corrosion. A thin film of evaporated gold on a pyrex or quartz slide was used as a semitransparent electrode. The photocurrent transient signal was recorded by means of Tektronix Type 531 oscilloscope with either plug-in unit Type E or Type 53D/54D. A d.c. voltage was supplied to the semitransparent electrode by means of a Keithley d.c. power supply, Model 240. A General Radio Co. Strobotac, Type 1531-A, was used as a pulsed light source (flash duration 1 to 3 microseconds).

Figure 2 shows the various masking arrangements used on crystals of *p*-chloranil in order to investigate the effect of screening different parts of the crystal–electrode system on the ambient vapor effects. Masking the various parts of the electrode system and the exposed crystal surface was achieved by the application of a thick film of "Hysol" epoxy resin to the areas of interest. When the electrode surface was masked, contact was made by means of thin copper wires attached to the electrode before application of the epoxy resin.

Results

In order to identify the site of ambient vapor induced carrier injection, bulk dark conductivity measurements were carried out on *p*-chloranil crystals exposed to various electron donor vapors in which various parts of the crystal electrode arrangement were masked from the ambient gas as shown in Fig. 2. Masking the electrodes considerably reduces the response to triethylamine and trimethylamine, slightly reduces the response to methylamine and hardly changes the response to ammonia (Table 1). Similar measurements, this time masking the unpainted portions of the crystal with epoxy resin as shown in Fig. 2b, showed no bulk conductivity response to the vapor of triethylamine, trimethylamine or methylamine. A slight response, $\rho_{\text{initial}}/\rho_{\text{final}} = 1.1$, was observed only on exposure to 120 mm Hg of ammonia.

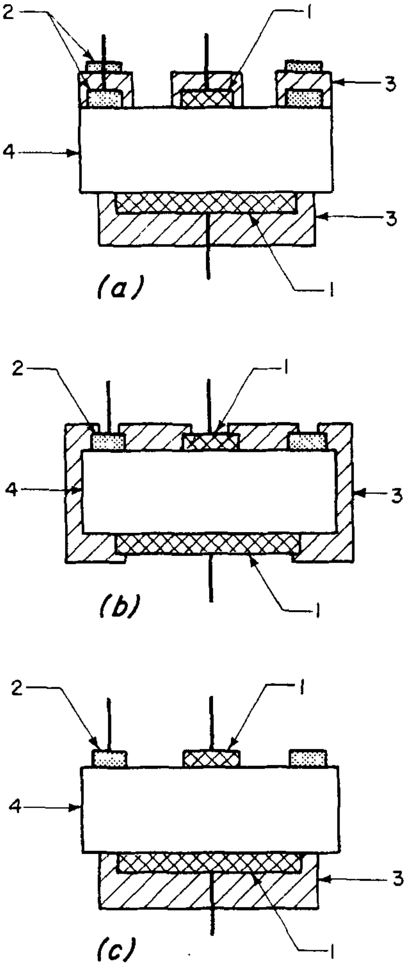

Figure 2. Cross sections of chloranil crystals with different masking arrangements. (a) Masking the electrode; (b) masking the unpainted crystal surface; (c) masking the individual electrodes. 1, electrode; 2, grounded guard ring; 3, epoxy resin coating; 4, crystal.

TABLE 1 Bulk Dark Conductivity Response of Chloranil to Amine Vapors with the Electrodes Masked

Ambient vapor	Pressure (mm Hg)	$\rho_{\text{initial}}/\rho_{\text{final}}$[a] Masked	$\rho_{\text{initial}}/\rho_{\text{final}}$[a] Unmasked
Ammonia	72	3.7	4.2
	24	2.9	1.8
	13	2.6	1.1
Methylamine	30	11.8	28.0
	13	7.3	21.5
	4	4.0	15.0
Trimethylamine	17	1.0	11.7
	11	1.0	10.3
	4	1.0	8.0
Triethylamine	11	1.0	88.0
	6	1.0	79.0
	2	1.0	65.0

[a] ρ_{initial} is the resistivity of the unexposed sample and ρ_{final} the new steady-state value attained after exposure to ambient vapor.

These results suggested that contact of ambient vapor with the exposed crystal surface and outer electrode surface is not an essential requirement for charge injection, but that the most likely site for charge injection is the space between the electrode surface and the crystal surface. In both masking arrangements *a* and *b*, the diffusion of molecules into this space is hindered and a reduction in charge injection is expected. The diffusion of ammonia, the smallest molecule, may be expected to be the least hindered explaining why the charge injection was comparatively unaffected in this case.

In order to obtain further evidence for the involvement of the electrode–crystal interface in ambient vapor induced charge injection processes, several experiments on the effect of electrode polarity on charge injection were carried out. In these experiments the effects of (a) electrode area symmetry (b) masking one electrode, as in Fig. 2c for example, and (c) the state of the electrode surface, i.e. the crystal surface on which the electrode is arranged, were explored. Variable results were obtained before the physical state of the electrode surface was allowed for in a systematic way. It was found that if both electrode surfaces were roughened, the bulk dark conductivity response was symmetrical with respect to electrode polarity whereas if only one electrode surface was roughened, a greater response was found when the electrode was at negative potential. This effect was found to be dominant in determining asymmetry of bulk dark conductivity response. Earlier asymmetric response results, which were thought to be due to the effect of electrode area asymmetry and masking asymmetry, were found to have actually arisen from the two electrode–crystal interfaces being different in roughness. Table 2 shows the bulk dark conductivity response for a chloranil crystal with both electrode surfaces roughened, and Table 3 shows the response with only the small area electrode surface roughened. When the large electrode surface was roughened and the crystal exposed to ammonia, the conductivity response was 1.7 with the electrode negative and 1.1 with the electrode positive.

TABLE 2 Bulk Dark Conductivity Response of Chloranil with Asymmetrical Electrodes and Both Electrode Surfaces Roughened

Ambient vapor	Pressure (mm Hg)	Polarity of small electrode	$\rho_{\text{initial}}/\rho_{\text{final}}$
Xylene	6	–	3.4
Toluene	6	–	1.3
Benzene	6	–	1.07
Benzene	6	+	1.36
Toluene	6	+	1.44
Xylene	6	+	3.4
Trimethylamine	20	+	18.5
Triethylamine	20	+	15.4
Triethylamine	20	–	15.4
Trimethylamine	20	–	16.6

These results can be interpreted as follows: the greater effect when the negative electrode surface is roughened arises because more molecules can diffuse into the electrode–crystal interface in

TABLE 3 Bulk Dark Conductivity Response of Chloranil with Asymmetrical Electrodes and the Small Electrode Surface Roughened

Ambient vapor	Pressure (mm Hg)	Polarity of small electrode	$\rho_{\text{initial}}/\rho_{\text{fina}}$
Ammonia	20	+	1.13
Methylamine	20	+	1.0
Trimethylamine	20	+	1.0
Triethylamine	20	+	1.0
Ammonia	20	−	1.84
Methylamine	20	−	6.0
Trimethylamine	20	−	3.44
Triethylamine	20	−	2.63

this case and participate in carrier injection, i.e. electron injection. These carriers then drift through the crystal to the positive electrode and cause the observed dark conductivity increase. When the roughened electrode is positive, ambient induced injected electrons will be immediately neutralized and will not contribute to the dark conductivity increases. In this case the observed conductivity increase will be the contribution from injection at the unroughened electrode surface. When both electrode surfaces are roughened a symmetrical response with regard to electrode polarity is obtained because the charge injection process takes place to a comparable extent at both electrodes. This appears to be the case even though the electrodes themselves are asymmetric in area.

These results strongly suggest that the most likely site for ambient vapor induced carrier injection into the bulk of organic crystals is the electrode–crystal interface. A possible explanation of the ambient vapor induced carrier injection can thus be considered in terms of the creation of a more "ohmic" contact which allows more carriers to pass into the crystal until space charge limitation controls the current level. An ohmic contact is here considered to be an injecting contact which allows an infinite reservoir of carriers to be available for injection into the crystal. A major limitation on current passing through the crystal is then the space charge set up by the injected carriers[5] and a superlinear dependence of current on voltage is expected.

To seek evidence for ambient vapor induced space charge limited currents, bulk dark current–voltage characteristics were investigated for both the anthracene–iodine system and chloranil–ammonia system. Bulk dark current–voltage studies on the chloranil–ammonia system showed that a similar current–voltage characteristic was obtained whether the crystal was in ambient electron donor vapor or not.[2] A higher current level was obtained in the case of crystal in ambient vapor but the form of the characteristic–linear behavior up to field strengths of 4×10^3 V/cm followed by a superlinear dependence of current on voltage at field strengths higher than this, was similar in all cases. If anything the ambient characteristic tended to deviate from linear behavior at slightly higher field strengths than the unexposed crystal characteristic. The superlinear region of the current–voltage characteristic for the unexposed crystals was interpreted as caused by space-charge-limited-trap-limited currents arising from carrier injection through an ohmic electrode. These data were analyzed to yield information on carrier trap densities and depths in chloranil.[6] The form of the characteristic in the case of crystal exposed to ambient gas suggested, however, that ambient vapor induced carrier injection was notresulting in space-charge-limited conditions below 4×10^3 V/cm; otherwise departures from linearity would have been observed below this field strength. Similar results obtained for the anthracene–iodine system showed that the onset of superlinear current–voltage behavior occurred at lower field strengths for the exposed crystals in this case. Figure 3 shows bulk dark current–voltage plots for the anthracene–iodine system. These results thus suggest that ambient vapor induced charge carriers in organic crystals do not cause space-charge-limited conditions at low field strengths but may at higher field strengths.

The effect of ambient vapor on the bulk dark conductivity of organic crystals was originally discussed as an effect on the charge carrier concentration rather than the carrier mobility. It was considered unlikely that surface effects could produce the profound

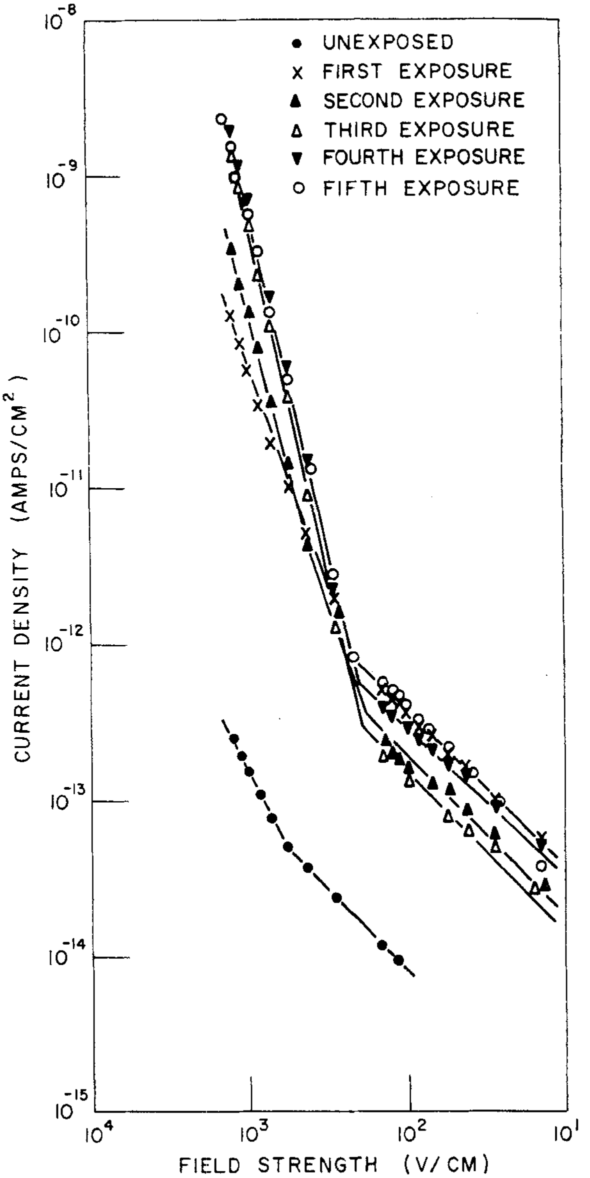

Figure 3. Bulk dark current–voltage relationships for anthracene crystals exposed to iodine vapor (0.2 mm Hg).

changes in crystal structure necessary to cause mobility changes of the required magnitude. In order to experimentally test the possible effect of ambient vapor on mobility, drift mobility determinations were carried out on anthracene crystals equipped with a grounded guard ring and exposed to an iodine–nitrogen gas mixture. The partial pressure of iodine vapor in 1 atmosphere of nitrogen was 0.2 mm Hg. These results were then compared to similar experiments in which the crystal was exposed to nitrogen only.

Figure 4 shows two typical hole photoconductivity pulses observed in an anthracene crystal perpendicular to the *ab* plane (a) in a nitrogen atmosphere and (b) in a nitrogen–iodine atmosphere.

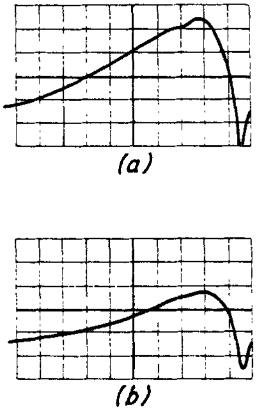

Figure 4. Pulsed hole photocurrent in an anthracene crystal. (*a*) Crystal in 1 atmosphere of nitrogen, 0.1 mV/large division, 20 μsec/large division; (b) crystal in 1 atmosphere of nitrogen containing 0.2 mm Hg of iodine vapor, 0.2 mV/large division, 20 μsec/large division. Applied voltage, 1000 V, crystal thickness, 2 mm.

Figure 5 shows a plot of hole drift time against the reciprocal of the applied voltage in the two atmospheres. Mobilities were evaluated from

$$\mu = \frac{d^2}{Vt}$$

where μ is the drift mobility, d is the crystal thickness, V is the applied voltage and t is the drift time. Hole mobilities ranged from 0.5 to 1.5 cm^2 /volt sec in agreement with literature values.[4,7,8] No discernible effect on the mobility was found on exposing the anthracene crystal to iodine, however, conclusively demonstrating that the observed effects on the bulk dark conductivity produced by iodine can be considered exclusively a charge carrier phenomenon.

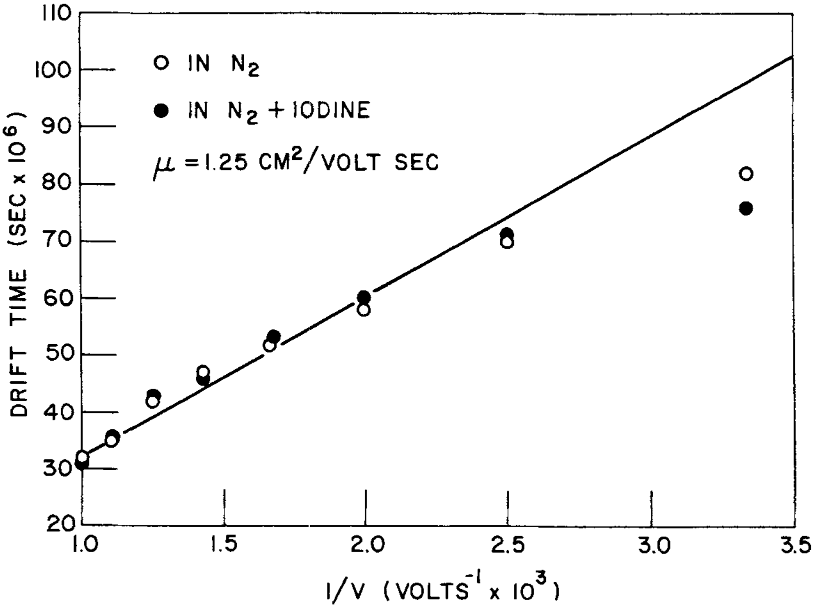

Figure 5. Hole drift time $-1/V$ plot for an anthracene crystal of thickness 2.1 mm.

Summary and Conclusions

The conductivity results obtained on masked samples and samples with treated electrodes suggest that the site of ambient induced carrier injection is at the electrode–crystal interface. The current–voltage data indicates that space-charge-limited current conditions are not being established at the lowest voltages even though the current level is higher than that of the unexposed crystal. At the highest voltages there is some evidence for ambient induced space-charge-limited currents particularly in the anthracene–iodine case. In this region, however, a superlinear dependence of current on voltage is obtained for the unexposed crystal, interpreted as due to space-charge-limited currents, which tends to obscure effects due to ambient vapor. Considering ambient induced conductivity phenomena in terms of an effect involving the electrode, i.e. the production of a carrier injecting contact, has thus some validity but it is apparent that space-charge-limited current conditions are not being produced by ambient effects alone. The most reasonable conclusion seems to be that ambient induced carrier injection involves the creation of a partially ohmic contact with concomitant partially space-charge-limited currents in the crystal. Similar conclusions have been reached by Bauser in an independent study on the anthracene–iodine system.[9]

The mobility studies on anthracene crystals in iodine ambient confirm that charge carrier mobilities are unaffected by ambient vapor, and the effects on bulk dark conductivity are caused by increases in the charge carrier concentration.

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