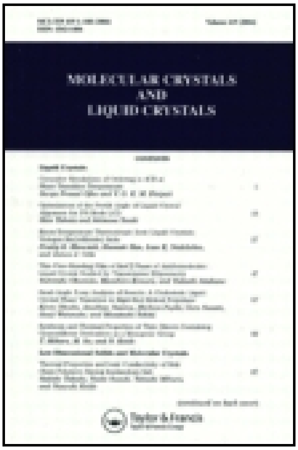

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On the Feasibility of Observing Photoemission from Metal Contacts into Anthracene

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On the Feasibility of Observing Photoemission from Metal Contacts into Anthracene

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Two processes can mask, partly or completely, photoemission from metal contacts into anthracene: carrier photoexcitation out of surface traps which are occupied under thermal quilibrium, and photoexcitation out of bulk traps which are continuously being filled by carrier injection from the contact under study. The first process is studied in this paper by photoconductivity measurements in the absence of contact effects. The photocurrents are shown to originate from hole photoexcitation out of surface traps. They are greatly influenced by surface treatments but even under the most optimal treatment the spectral yield is similar both in magnitude and threshold to yield curves obtained by several workers and attributed to photoemission. As to the second process, the arguments presented suggest that with contacts of alkali and alkaline-earth metals (electron injectors) and gold (hole injector) the reported yield curves are probably associated with photo-enhanced space-charge-limited currents.

A critical examination of the available data indicates that photoexcitation out of surface or bulk traps in anthracene, rather than contact photoemission, plays the dominant role in some cases while in others this possibility cannot be ruled out. The data and arguments presented here point to the necessity of carefully checking the contribution of surface generation and/or contact injection before any photoemission studies are undertaken.

INTRODUCTION

In the past several years a number of workers have reported on measurements of hole and electron photoemission from metal contacts into single crystal anthracene. Such measurements, if successful, can yield valuable information on the band structure of anthracene. In particular they can lead to a determination of the energy band gap which, in spite of extensive efforts, has not yet been reliably determined.

Hole photoemission from different metal contacts into anthracene was first reported by Williams and Dresner.[1] These workers could not detect electron photoemission. Later, Baessler *et al*[2] and Many *et al*[3] reported on measurements of electron photoemission from alkali and alkaline-earth metal contacts. Many *et al*[4] soon realized, however, that the contacts used were electron injecting (in the dark) and that the photocurrents measured were in reality photo-enhanced space-charge-limited currents arising from optical release of trapped electrons. (It turned out that the traps involved were located essentially at one discrete energy level so that such measurements proved to be equally effective in deriving information on the conduction-band structure as photoemission studies would have been.) Baessler *et al*[5-8] and later Dresner[9] and Donnini and Abetino[10], on the other hand, still maintained that the photocurrents they had observed were due to electron photoemission. Furthermore, Vaubel and Baessler[11] claimed that they were able to observe both electron and hole photoemission from the *same* metal contact (Ce or Mg) into anthracene. Using the two threshold energies for electron and hole photoemission they estimated the energy gap of anthracene as 3.72 ± 0.03 eV. Recently, Caywood[12] has reviewed the available data on photoemission into anthracene. His analysis supports essentially the interpretation given by Baessler and co-workers.

In the present paper the feasibility of observing carrier photoesmission from metal contacts into anthracene is critically examined. To this end photoconductivity in anthracene for non-absorbed light (photon energies well below 3.15 eV, the singlet absorption peak) was studied in detail. Such photoconductivity can arise from contact photoemission as well as from carrier photoexcitation out of surface and bulk traps. Most of the measurements reported so far did not very well distinguish between these two processes, and the interpretation of the data was largely based on the assumption that carrier excitation out of traps plays a negligible role. In order to check this assumption directly we employed blocking contacts in which thin mylar sheets were interposed between the metal electrodes and the anthracene sample. (The use of conducting-glass electrodes in direct contact with the sample's surfaces was found to be equally effective in eliminating contact effects.) Any photocurrents observed under these conditions can originate from surface and/or bulk traps only. It was found that such photocurrents were greatly influenced by surface treatment and in all cases they were far from negligible. The lowest photocurrents obtain after prolonged etching in benzene, when the photocurrent threshold is about 2 eV. It has been established that even in this case the photocurrent originates almost entirely from hole photoexcitation out of surface traps. The other surface treatments used resulted not only in higher hole photocurrents but also in shifts of the threshold towards lower photon energies. Photocurrent/voltage measurements carried out after different surface treatments were used to determine in each case the absolute magnitude of the spectral yield for hole photoexcitation, as well as the surface recombination velocity characterizing the hole re-trapping process.

The spectral yield curves obtained in these measurements are similar both in magnitude and threshold to most of the yield curves reported for non-blocking contacts and attributed to contact photoemission. The similarity is particularly striking between our photocurrent yield curves and those obtained by Vaubel and Baessler[11] in estimating the band gap. It thus appears that contact photoemission into anthracene may well be masked by hole photoexcitation out of surface traps. We believe that the contribution of such surface generation should be carefully checked prior to the deposition of the metal electrode used in the photoemission studies, if any significance is to be attached to the data obtained.

Another effect discussed in this paper which may completely mask internal photoemission is carrier injection from the metal contact under study. Here photoexcitation out of bulk traps, which are continuously being filled by injection from the contact, may play the dominant role in the observed photocurrent. Typical examples of injecting contacts are alkali and alkaline-earth metals[4] (electron injectors) and gold[13] (hole injector).

EXPERIMENTAL

The experimental setup used was similar to that described previously.[4] Measurements were carried out on Harshaw crystals as well as on crystals grown in this laboratory from the melt. The samples were cut out from the ingot by a wire saw and subsequently polished to the desired thickness (0.3–1 mm). The various surface treatments included: prolonged etching in benzene, submersion in water, grinding with sandpaper, exposure to HCℓ vapour and ion sputtering in an atmosphere of air (0.1–0.2 torr). After each surface treatment, the sample was enclosed in a sandwich-type cell[4] with conducting-glass electrodes. Thin (12μ) mylar sheets were interposed between the transparent electrodes and the sample in order to prevent any hole and electron injection from the electrodes either in the dark or under illumination (photoemission). Careful measurements have revealed that even direct contact between the conducting-glass electrodes and the sample's surfaces gave neither dark injection nor photoemission, so that the mylar sheets could be omitted.

The sample holder and the current and photocurrent measuring circuits were as described previously.[4] The sample was illuminated through the transparent conducting-glass electrodes. The optical system used for illumination consisted of a 150W Tru-flector Sylvania lamp and a Jarrel-Ash grating double monochromator. With a slit opening of 1 mm used in the present measurements, the spectral width was about 20A. All measurements were carried out at room temperature under an ambient pressure of 10^{-5} Torr.

RESULTS

In this work we have studied photoconductivity in anthracene for non-absorbed light (photon energy $h\nu < 3$ eV) as well as at the singlet absorption peak ($h\nu = 3.15$ eV). One of the primary objectives has been to eliminate carrier injection from the contacts into the anthracene sample, by internal photoemission or through any other processes. To this end blocking contacts were initially employed in the form of thin mylar sheets interposed between the (transparent) electrodes and the two surfaces of the sample. In this manner any photocurrent measured must originate entirely from photoexcitation in the surface and/or bulk of the sample. It was subsequently realized, however, that the mylar sheets were unnecessary: under the proper ambient conditions the conducting-glass electrodes, when in direct contact with the sample's surfaces, do not inject carriers either in the dark or under illumination. This is illustrated in Figure 1 where the spectral response of the photocurrent yield is shown for the case of direct contact (full symbols) and with mylar spacers (open symbols). The comparison is given for our melt-grown crystals (circles) as well as for Harshaw crystals (triangles). In all cases the measurements were carried out after the sample had been etched in benzene for fifteen minutes. Such a procedure has

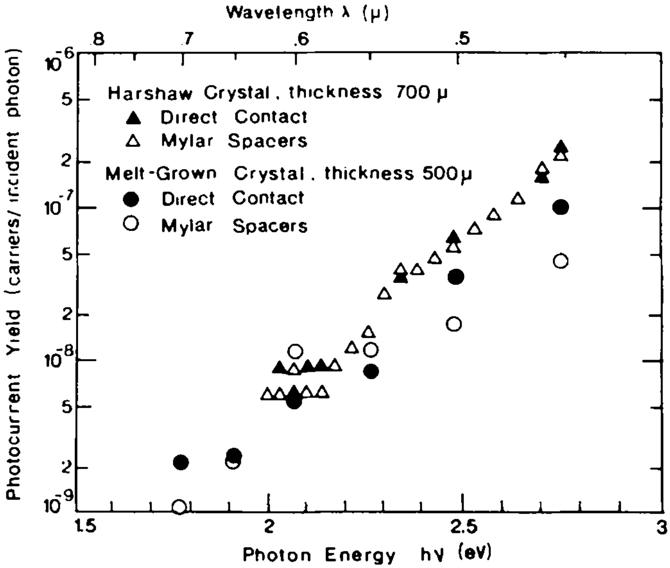

FIGURE 1 Spectral response of photocurrent yield obtained with mylar spacers (open symbols) and for direct contact between conducting-glass electrodes and sample (full symbols). Comparison is made for Harshaw and our melt-grown crystals. Applied voltage (500 V) above that required for photocurrent saturation.

been found to result in the lowest photocurrents. In all the measurements the applied voltage across the sample was 500 V, well above the voltage for which the photocurrent saturates (see below). It should be noted that the photocurrents here, as well as those described below, are directly proportional to the light intensity (i.e., the spectral yield is independent of light intensity).

It is evident from Figure 1 that there is no significant difference between the spectral yield curves obtained with or without mylar spacers. The differences of up to a factor of two or so are within the limits of reproducibility obtained on the same sample after consecutive but identical surface treatment. Thus the conducting-glass electrodes are not involved in the observed photocurrents any more than when mylar spacers are interposed. This means that, firstly, no carrier photoemission takes place from the conducting-glass electrodes and, secondly, that those electrodes are non-injecting in the dark. Any (dark) injection would give rise to photo-enhanced currents under illumination[4] (see Figure 7 below) and hence to higher photocurrents than for the case of blocking contacts. We conclude, therefore, that in both cases the source of the photocurrent is surface or bulk traps which are occupied under thermal equilibrium conditions. It should be noted that the triplet absorption spectrum is not reflected in the yield curves, indicating that *direct* optical excitation out of traps is the dominant mechanism. This is in contrast to photoexcitation of electrons out of bulk traps where de-trapping by interaction with triplet excitons plays a major role.[4]

Measurements with mylar spacers are inconvenient because of polarization effects. It was therefore decided to omit the spacers and use conducting-glass electrodes in direct contact with the sample in most of the subsequent measurements.

The similarity between the spectral yield curves for Harshaw crystals and for crystals grown (from the melt) in this laboratory, suggests that the photocurrents originate from photoexcitation out of surface rather than bulk traps, the latter being expected to be different in the two types of crystals. This is shown to be indeed the case by the data of Figure 2. Here the voltage dependence of the photocurrent yield for non-absorbed light ($h\nu = 2.48$ eV) is plotted for a thick sample (2 mm) and after the sample's thickness has been reduced by more than an order of magnitude (0.16 mm). In both cases the surfaces have undergone identical treatments (benzene etching). Both curves are seen to be symmetrical with respect to the voltage polarity, as to be expected from the symmetry of the experimental configuration (the sample is uniformaly illuminated). What is much more significant, however, is that the curves saturate at higher voltages and that the saturated yield values are much the same for the thin and thick samples. The saturation level represents the rate of carrier photoexcitation from traps. In this limit each photo-generated carrier is collected before it is re-trapped. The common saturation level for the two samples immediately indicates therefore that the *total* number of traps out of which the carriers are

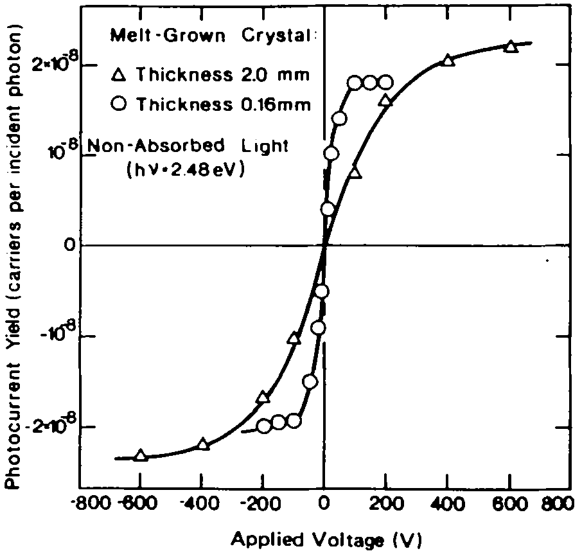

FIGURE 2 Photocurrent yield *vs.* applied voltage for benzene-etched samples of different thicknesses. Illumination with non-absorbed light ($h\nu = 2.48$ eV).

photoexcited is the same. Since the thickness of the samples are grossly different, this means that bulk traps are not involved, the major contribution arising from photoexcitation out of surface traps.

That surface generation is the dominant process is also apparent from the shape of photocurrent-yield curve. For bulk excitation (and trapping) the spectral yield saturate when the Schubweg $\mu\tau(V/L)$ (where μ is the carrier mobility, τ is the trapping time and V the applied voltage) becomes comparable to the sample's thickness L. The two curves in Figure 2 should then saturate at the same point when the yields are plotted against V/L^2. This is not the case as can be seen by inspection of Figure 2. When the photoexcitation (and trapping) takes place at the surface, on the other hand, saturation should occur for the same applied *field* ($E = V/L$). It can readily be shown[14] that the spectral yield η is then given by

$$\eta = \eta_s (1 + s/\mu E)^{-1} \qquad (1)$$

where η_s is the saturation level of the yield and s is the surface recombination velocity characterizing carriers trapping at the surface. Eq. (1) assumes that only one type of carrier is involved and that bulk excitation and trapping are negligible.

In Figure 3 the data in Figure 2, as well as results obtained on other samples (which received the same surface treatments), are shown as plots of the normalized spectral yield η/η_s against applied field $E = V/L$. The curve is a representation of Eq. (1) with $s/\mu = 10^3$ V/cm, the value found to give the best fit. It is seen that all the experimental points are well accounted for by the theoretical curve, the variation in the values of s/μ for the different samples being less than a factor of two. The variation in the saturation level η_s (indicated in the figure) is also small. These features indicate that the density and type of the surface traps involved in the photoexcitation and re-trapping processes are essentially the same in all the samples. Finally, the good fit between the experimental points and Eq. (1) suggests that only one type of carrier is involved (unless, of course, s/μ is the same for both carrier types, which is unlikely).

One way of determing the type of carrier involved is the use of strongly absorbed light. In this manner the carriers are generated very close to the illuminated surface, photoexcitation at the other surface being completely eliminated. Holes or electrons can then be swept into the sample by a proper choice of the voltage polarity. In Figure 4 the photocurrent/voltage characteristics (taken on a benzene-etched sample) are compared for non-absorbed light (a) and for strongly absorbed light (b). Figure 4(a) is similar to Figure 2, photoexcitation taking place at both surfaces. In Figure 4(b), on the other hand, photogenerated holes are swept into the bulk when the illuminated surface is positive (to be

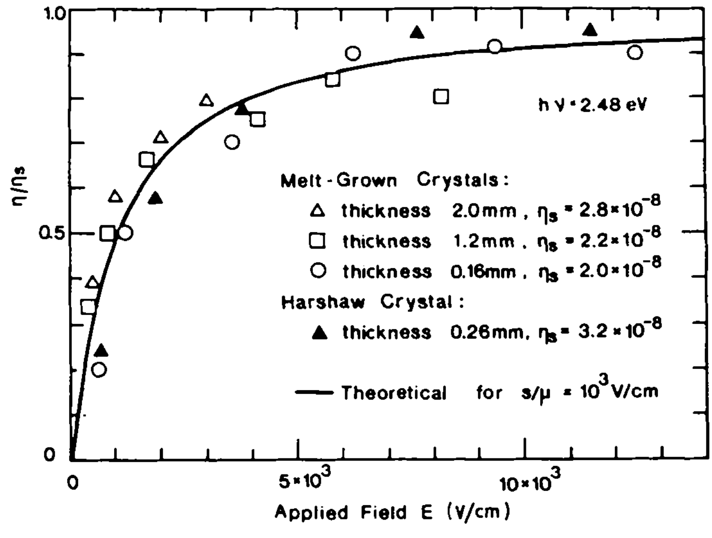

FIGURE 3 Normalized photocurrent yield η/η_s *vs.* applied field for different benzene-etched samples. Illumination with non-absorbed light ($h\nu = 2.48$ eV). Solid curve represents Eq. (1) with $s/\mu = 10^3$ V/cm.

designated henceforth as the positive polarity), while in the negative polarity photogenerated electrons are swept in. The voltage characteristics of the hole photocurrent are very similar to those for non-absorbed light (Figure 4a), both yielding much the same value of *s*. (The absolute magnitude of the photocurrent is of course much higher for strongly absorbed light.) The electron photocurrents, on the other hand, are about three orders of magnitude lower and are characterized by a much larger *s*. As is well known[15] the mechanism of carrier excitation at the surface in this spectral range is the interaction of photogenerated singlet excitons with occupied surface traps. Hence it is very reasonable to assume that the same surface traps are involved in the surface photoexcitation process under strongly-absorbed and non-absorbed light. In view of the observation that the electron photocurrent is much smaller than the hole photocurrent

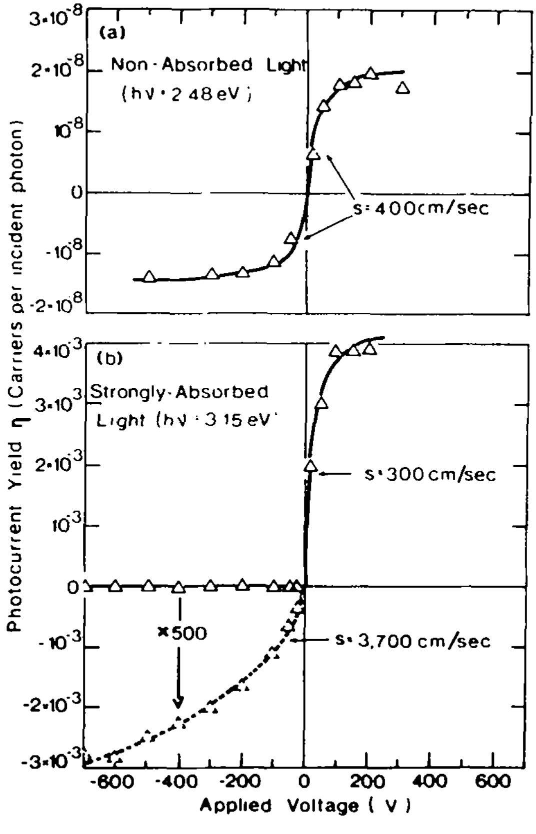

FIGURE 4 Photocurrent yield η *vs.* applied voltage for non-absorbed (a) and strongly-absorbed light (b). Dashed curve in (b) represents electron photocurrent after multiplication by factor of 500. Benzene-etched Harshaw sample (thickness 340 μ).

and is characterized by a much larger value of s, one may conclude that the chief contribution to the photocurrent under *non-absorbed* light is hole conduction. The contribution of electrons photogenerated at the counter surfacer (adjacent to the negative electrode) can safely be neglected.

The values of s quoted in the figure (for holes and electrons) were obtained from the parameters s/μ using the value of the hole or electron mobility in the crystallographic direction under study (normal to the (*ab*) plane), namely 0.5 or 0.4 $cm^2/V{\cdot}sec$, respectively.

It might be worthwhile mentioning at this point that for strongly adsorbed light both the hole and electron photocurrents are about one order of magnitude smaller in our melt-grown crystals compared to the Harshaw crystals (in both cases the surfaces were benzene etched). This difference in behaviour has not been investigated further. It may be due to the different crystallographic faces studied in the two cases: the surfaces were parallel to the (*ac*) plane in the samples cut from our crystals and parallel to the (*ab*) plane in the samples cut from the Harshaw crystals.

We now consider the effect of surface treatment on the photocurrent. As was pointed out above, prolonged etching in benzene gave the lowest photocurrents and the results shown so far were for such treatment. All other surface treatments applied resulted in higher photocurrents. These included prior dipping in de-ionized water, exposure to $HC\ell$ vapour, ion sputtering and mechanical damage to the surface. Even the slight mechanical damage incurred during insertion of a benzene-etched sample into the sample holder may enchance the photocurrents by a factor of 2 or 3. This is evidenced by measurements taken after removal and re-insertion of the sample into the holder. In order to minimize such effects extreme care in handling the sample is necessary.

We shall confine the discussion to the water treatment because several workers[1, 5–9] have used water as the transparent electrode. The effect of such treatment on the voltage dependence of the photocurrent yield is shown in Figure 5. The melt-grown sample was first etched in benzene and the photocurrent characteristics were determined for both non-absorbed and strongly absorbed light (squares in Figures 5). The results are similar to those shown above. Subsequently, the sample was taken out of the sandwich-type cell and a drop of de-ionized water was applied to one of the surfaces for about an hour. The water drop was then absorbed by filter paper and the sample re-mounted in the cell. The results obtained after this treatment are represented by the triangles in Figure 5. Consider first the case of non-absorbed light (Figure 5a). The hole photocurrent originating from the water-treated surface is seen to have increased by a factor of about 25, with no significant change in the hole recombination velocity. In the reverse polarity (water-treated surface negative), on the other hand, the photocurrent remained unchanged. This means that the electron photocurrent originating from the treated surface is still negligible compared to the hole photocurrent originating from the opposite (benzene-etched) surface.

The effect of the water treatment on the hole photocurrent is similar with highly absorbed light (Figure 5b): a tenfold enhancement in current with little difference in *s*. The electron photocurrent (water-treated surface negative) is again small and the yield scale had to be blown up in order to display the voltage characteristics (Figure 5c). Here, as well, the water treatment gives rise to a tenfold enhancement in yield, but now there is also a considerable enhancement in the electron recombination velocity *s*.

The observed enhancement in the saturated hole and electron photocurrents by the water treatment can only mean a corresponding enhancement in the density of surface hole and electron traps out of which the respective carriers are photoexcited. At the same time, the insensitivity of *s* to the water treatment in the case of the hole photocurrent indicates that the hole states responsible for trapping are different from those out of which the holes are photoexcited. In the

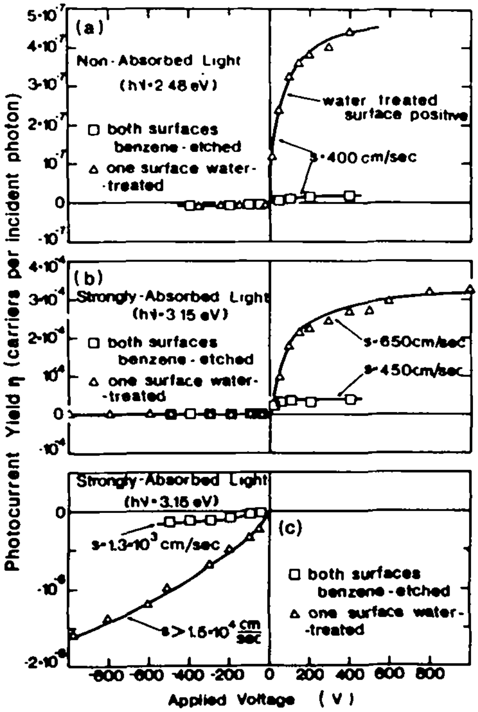

FIGURE 5 Photocurrent yield η *vs.* applied voltage for non-absorbed (a) and strongly-absorbed light (b). Electron photocurrent (b) is replotted on expanded yield scale in (c). Squares correspond to benzene-etched surfaces, triangles – to one surface water treated. Solid curves represent Eq. (1) with indicated valued of *s*. Melt-grown sample (thickness 1.9 mm).

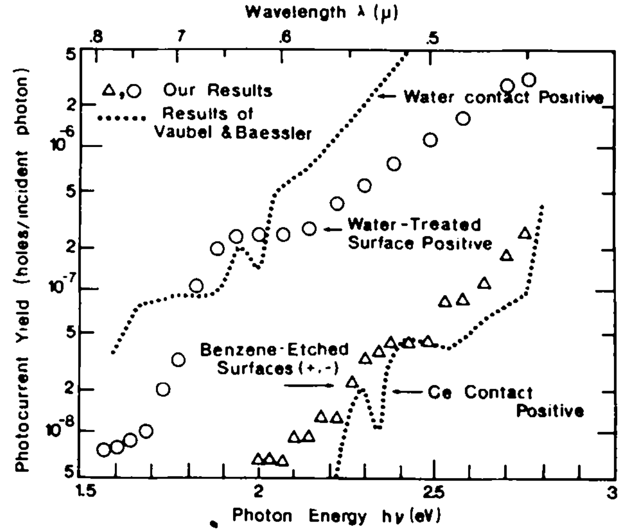

FIGURE 6 Spectral response of saturated photocurrent yield for benzene-etched surfaces (triangles) and for water-treated surface when positively biased (circles) obtained on Harshaw sample. Dotted curves represent "photoemission" data obtained by Vaubel and Baessler on Harshaw sample for Ce contact positive (lower curve) and for water contact positive (upper).

case of the electron photocurrent, on the other hand, the saturated photocurrent and *s* are enhanced by nearly the same factor, suggesting that the same set of states is involved in both the photoexcitation and trapping processes.

The effect of the water treatment on the spectral distribution of the photocurrent yield is shown in Figure 6. The triangles represent the saturated yield (for either voltage polarity) obtained for benzene-etched surfaces (Harshaw crystal). As has been shown above this yield curve corresponds to hole photocurrents orginating from photoexcitation out of surface traps. The circles represent the yield after one of the surfaces has been water-treated, this surface being made positive in the measurement. [For the opposite polarity the points fall very close to those obtained when both surfaces were benzene-etched (the triangles)]. It is seen that the hole spectral yield for a water-treated surface lies considerably higher than that for the benzene-etched surface, while the threshold for detectable photocurrents moves towards lower photon energies (from about 2 eV to 1.5 eV).

Both the magnitude and threshold of the spectral yield of the hole photocurrent in a water-treated surface depend on the length of exposure of the surface to water and on the prior surface condition. The results in Figure 6 (circles) represent a typical but by no means unique behaviour of the water-treated surface. As to the benzene-etched surfaces, we believe our results (triangles) correspond to the lowest surface trap density that can be achieved on anthracene by ordinary surface-treatment procedures. To the extent that surface treatments are described in the papers on photoemission into anthracene, none seems to be markedly different from those tried in the course of this work. We conclude, therefore, that unless spectral yield curves reported on anthracene lie considerably above those shown in Figure 6, they cannot be reliably interpreted as originating from a process other than hole photoexcitation out of surface traps. In particular one has to examine very carefully data obtained with various metal contacts and attributed to photoemission from the contacts into the anthracene sample.

As an example we reproduce in Figure 6, as nearly as could be derived from the published data, spectral yield curves reported by Vaubel and Baessler[11] for a Harshaw sample with a cerium contact on one surface and a water contact on the other. As can be seen, the yield curve with the Ce contact positive, which was attributed by those workers to hole photoemission from Ce into the sample, is very similar in magnitude, shape and threshold to our data (triangles) for the benzene-etched surfaces. Our yield curve has been shown to be due to surface hole traps and one is lead to doubt seriously Vaubel and Baessler's claim of photoemission. Similar doubts exist concerning Vaubel and Baessler's yield curve for the case of Ce contact negative (upper dotted curve). In this configuration the water contact is positive and the enhancement in yield may well be similar to that observed by us for water-treated surfaces. In fact, our points (circles), obtained after such treatment, again lie very close to Vaubel and Baessler's curve. We therefore feel that Vaubel and Baessler's determination of the energy band gap of anthracene on the basis of the thresholds of the dotted curves is very doubtful.

Photoexcitation of holes at the anthracene surface proper can thus be a serious pitfall in measurements of internal photoemission. A contact that is injecting in the dark is another possible pitfall. In this case photoexcitation out of bulk traps, which are continuously being filled by injection from the contact, may well overshadow direct photoemission from the contact.[4] Although photoemission under these conditions cannot be ruled out in some of the data presented, we feel that more attention should have been given to the other possible mechanism (photoexcitation out of bulk traps), particularly in those cases where there is a likelihood that the contacts employed may be injecting. Many of the contacts used in studies of photoemission, such as alkali and alkaline-earth metals are known[4, 16] to be electron injecting into anthracene while others, such as gold, were shown to be hole injecting.[13] In fact, even the free surface can be injecting. For example, a sand-blasted surface was found to be a good injector of holes. Even the well-behaved benzene-etched surface can become a hole injector under extremely dry conditions.

We consider, as an example, the data of William's and Dresner.[1] These workers used a gold contact which, as has been mentioned above, can be a hole injector. Although it appears possible that the data reported in this instance do indeed represent photoemission, there are still some doubts which should not be overlooked. In Figure 7 we have reproduced Williams and Dresner's results for the spectral photocurrent yield (lower curve). The absolute magnitude of the field is uncertain, firstly, because only its order of magnitude has been reported by the authors. More important still, the photocurrent was not measured under voltage saturation conditions. The upper curve represents our results obtained for the yield of the photo-enhanced space-charge-limited current obtained with a CuI hole injecting contact. These measurements are similar to those reported previously for photo-enhanced electron currents.[4] One cannot but wonder at the similarity in the structure of the two curves: the identical thresholds and the two kinks (marked by arrows) occurring at exactly the same photon energies.

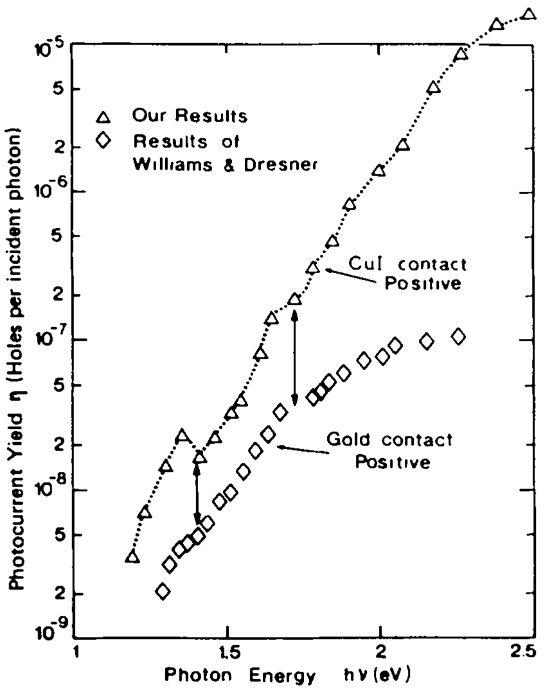

FIGURE 7 Comparison of spectral yield of photo-enhanced space-charge-limited hole current obtained with a CuI hole-injecting contact (triangles) with the yield obtained by Williams and Dresner with a gold contact and attributed to hole photoemission (squares). Applied fields were 10^4 and 2×10^3 V/cm in former and latter measurements, respectively. Arrows mark kinks in curves occuring at same photon energies.

DISCUSSION

In this work we have studied photoconductivity in anthracene in the absence of contact effects. Contact effects were eliminated by introducing mylar spacers between the electrodes and the sample's surfaces or, what was found to be equally effective, by using conducting-glass electrodes in direct contact with the surfaces. The observed photocurrents were shown to be very sensitive to surface treatment. The lowest photocurrents were obtained after prolonged etching in benzene. It has been established that even in this case the photocurrents under non-absorbed light (when both surfaces of the smaple are illuminated) in both Harshaw and our melt-grown crystals originate almost entirely from hole photoexcitation out of surface traps. Bulk excitation and trapping is negligible, as is the contribution of photoexcited electrons from surface (and bulk) traps. Electron photocurrents can be detected only for strongly-absorbed light at the negatively-biased surface, when no light can reach the opposite, positively-biased surface to photoexcite holes there. Such photocurrents are two-three orders of magnitude lower than for the reverse polarity, when the photoexcited holes at the illuminated surface (positive) are swept into the sample.

For non-absorbed light, holes are generated at the two surfaces by direct photoexcitation out of surface traps. De-trapping by photogenerated triplet excitons does not play a significant role. For strongly absorbed light, on the other hand, interaction of trapped holes (and electrons) with photogenerated singlet excitons appears to be the dominant mechanism in the carrier excitation process. For all surface treatments, saturation of the hole photocurrent (and in most cases of the electron photocurrent as well) is readily attainable at moderate voltages. This permitted the determination of the absolute magnitude of the quantum yield η_s of the excitation processes under different surface conditions. Analysis of the photocurrent/voltage characteristics yielded the hole or electron surface recombination velocity s associated with surface trapping. The yield η_s was found to vary appreciably with surface treatment, indicating that the density of surface traps is very sensitive to the treatment applied. For benzene-etched surfaces, the yield for hole photogeneration near threshold (~2 eV) is about 5×10^{-9} carriers per incident photon, and increases more or less exponentially at higher photon energies. The hole recombination velocity is several hundred centimeters per second and is not very sensitive to surface treatment.

The measurements described in this paper show that over an appreciable spectral range of non-absorbed light ($h\nu \gtrsim 2\,\text{eV}$) it is very difficult, if at all possible, to eliminate photocurrents originating from surface traps. Hence spectral-yield curves obtained with various metal contacts and attributed to photoemission from the contacts into anthracene should be examined very carefully. It should be stressed that the main usefulness of the photoemission technique is restricted to those situations in which both electron and hole photoemission can be observed from the *same* metal contact. In these cases the energy gap can be determined, it being given by the sum of the energy thresholds for the two photoemission processes. Otherwise, it may be more advantageous to study photo-enhanced space-charge-limited currents obtained with an electron (or hole) injecting contact. In this configuration the photocurrent originates from photoexcitation out of bulk traps which are being continuously filled by carrier injection from the ohmic contact. If the traps are essentially discrete in energy, the structure of the conduction- (or valence-)band can be more accurately derived from the yield curves than in the case of photoemission, when the entire Fermi sea in the metal can participate in the excitation process. Results obtained in this manner on the conduction-band structure of anthracene have already been reported,[4] while data pertaining to the valence band[17] was published recently. The drawback in such measurements is that there is no simple way of determining the energy gap, since the energy separation between the electron and hole traps is unknown.

Vaubel and Baessler[11] were the only workers who have attempted to derive the energy gap of anthracene by the photoemission technique. If correct, such a determination yields one of the most fundamental parameters of anthracene. It was for this reason that Vaubel and Baessler's results were discussed above at some length (see Fig. 6). Our data and the arguments presented there throw serious doubts as to the interpretation of these workers. More recently, Baessler and Killesreiter[18] reported similar measurements but with the water electrode replaced by conducting glass and the Ce electrode illuminated by a He–Ne laser ($h\nu = 1.98$ eV). The photocurrents with the Ce contact negative were high compared to those with the Ce contact positive, an observation which was claimed to support the previous photoemission interpretation.[11] Unfortunately, however, nothing is stated about the condition of the surface in contact with the conducting glass. As was shown above the surface may be the source of appreciable hole photocurrents. On the other hand, the possibility of electron photoemission from the Ce contact cannot be ruled out in this experiment. However, the question of whether Vaubel and Baessler really detected *hole* photoemission from Ce (when positively biased) is still unanswered and the doubts concerning their determination of the energy gap have not been removed.

We consider now data reported by Williams and Dresner.[1] Except for contacts of gold and silver, the other metals used gave much the same threshold for the hole photocurrent (1.86, 1.6 and 1.97 eV for Aℓ, Pb and Mg, respectively). The quantum yield near threshold was of the order of 5×10^{-9}. As was shown above both the thresholds and the yields are very similar to those obtained by us after benzene etching (the optimal treatment) and shown to be due to surface generation of holes. Hence it is likely that Williams and Dresner observed surface-generated rather than photo-emitted hole currents. The small differences in thresholds for the different metal contacts may well be due to different surface conditions. The fact that the shift in the threshold is inconsistent with the change in the work function of the metals supports this conclusion.

Williams and Dresner's results for a gold contact bring us to a consideration of a second effect that can mask photoemission, namely, contact injection. We have no means of assessing whether the yield curves obtained by these workers originate from hole photoemission from the gold contact or whether they represent photo-enhanced space-charge-limited currents. However, the fact that hole injection from gold into anthracene (in the dark) is readily obtainable [13] and the similarity of their yield curve and that obtained by us with a hole-injecting contact (see Fig. 7) seem to point towards the second possibility.

One can readily derive a rough limit for the photon energy below which carrier injection from the contact should be expected to mask photoemission from the contact. The thermionic emission over an energy barrier ϕ is given by the Richardson formula[19] $AT^2 \exp(-\phi/kT)$ where $A \approx 100$ A/cm^2, T is the absolute temperature and k is Boltzmann's constant. The maximum photoemission current can be estimated as follows. Typically, the photon flux out of a monochromator is $10^{15} - 10^{16}$ cm^{-2} sec^{-1}, while a reasonable figure for the quantum efficiency for photoemission is 1%. Hence one can expect a value of about 10^{-6} A/cm^2 for the photoemission current density. This becomes comparable to the thermionic emission current (at room temperature) when the barrier is 0.7–0.8 eV.

Caywood [12] points out that the actual thermionic currents should be expected to be much smaller because of the strong carrier scattering in anthracene[20] and possibly also because of trapping and space-charge effects. This is true but such processes should reduce the photoemission current by the *same* factor. Hence the above estimate for the limiting value of the barrier (0.7–0.8 eV) is not altered by scattering and trapping effects. In other words, irrespective of the processes taking place in the crystal, it is doubtful whether any observed photocurrent threshold below about 0.8 eV can be attributed to photoemission. Baessler and Vaubel[2] interpreted the photocurrent threshold of 1 eV obtained with a sodium electrode as the photoemission threshold. If so, this threshold represents also the energy barrier for thermionic emission. Accordingly, Caywood [12] concludes that thermionic emission is negligible which in itself, is probably true, a 1 eV barrier being larger than the above-estimated limit. However, apart from the photocurrent data, there is no evidence whatsoever that the barrier for thermionic emission is indeed 1 eV. The barrier may well be considerably lower than 0.7 eV so that the thermionic current is high notwithstanding the strong electron scattering. In other words, the sodium contact can easily be injecting (ohmic) and the low dark currents observed by Baessler and Vaubel[2] are trap-controlled space-charge-limited currents and not contact-limited currents. In this case, the measured photocurrents would be nothing else but photo-enhanced space-charge-limited currents,[4] with the 1 eV threshold representing the depth of the bulk traps involved.

A clear indication for an injecting contact is the observation of decaying photocurrents in the reverse polarity (non-injecting mode) *after* the sample has been maintained (in the dark) under the forward (injecting) polarity. It is through such tests that mercury amalgams of alkali and alkaline-earth metals, as well as a Na–K alloy, were shown to be electron injectors[4]. It should be pointed out, however, that the lack of observable reverse currents is no indication that the contact used is non-injecting. For one thing, the traps involved may be shallow such that the carriers are thermally bleached in the time interval it takes to measure the reverse current (usually several seconds). Yet optical release out of such shallow traps may give rise to photo-enhanced currents in the forward polarity, when the injecting contact continuously refills the traps. Secondly, the trap concentration may be very high so that trapping occurs very close to the injecting contact. In this case the contribution of optical de-trapping to the reverse photocurrent might be too small to be detectable.

In a series of papers Baessler *et al*[2,5-8,11] presented photocurrent yield curves obtained in anthracene with alkali and alkaline-earth metals, and attributed to electron photoemission from these contacts. It appears that the magnitudes and thresholds of the photocurrents for the different metals vary consistently with the changes in the work function, indicating that photoemission does play a role. Moreover, no decaying photocurrents could be detected (although it is not clear whether the measurements were taken *after* the prior application–in the dark–of a forward voltage). On the other hand, it is very difficult to understand why these metals were non-injecting in the experiments of Baessler and co-workers, whereas they definitely were in those of Many *et al.*[4] In fact, in a later publication Baessler and Vaubel[8] admit that Ca "slightly injects to solution-grown crystals". Moreover, it is very strange that their yield curves are very similar both in shape and magnitude to those reported by Many *et al*[3,4], where the photocurrents were definitely proved to originate from optical release of filled bulk traps. De-trapping was shown to occur by direct excitation at low photon energies and mainly by interaction with photogenerated triplet excitons at higher energies. In fact, the triplet absorption spectrum is clearly reflected in the yield curves of both Many *et al*[3,4] and Baessler *et al*[2,5] (provided that in the latter case the experimental points and not the smoothed out yield curve are considered[16]). In both cases the positions of the peaks match accurately those of the triplet absorption spectrum. Hence, attributing this structure, as Baessler and co-workers[5] do, to *direct* optical release of electrons trapped at surface states is very doubtful. It is much more likely that de-trapping by triplet excitons plays the major role in the data of Baessler *et al*[2,5], just as it does in the yield curves of Many *et al.*[4] *The traps involved must be bulk traps since, as has been pointed out by Baessler and co-workers*[5] themselves, de-trapping of occupied surface states by triplet excitons should be negligible. The important contribution of de-trapping of *bulk* traps by triplet excitons was subsequently observed directly by Weisz *et al*[21] by comparing yield spectra obtained with steady light to those measured with light pulses short compared to the triplet lifetime.

Dresner[9] presented a yield curve obtained for an anthracene surface having "well reacted anthracene complexes with K and Na", which he too attributed to electron photoemission. The threshold of about 0.8 eV obtained is too close to the limit estimated above (0.7–0.8 eV). Also, Dresner does not mention reverse-photocurrent measurements. It appears likely that here as well optical excitation out of bulk traps plays an important, if not the dominant role in the observed photocurrent.

In conclusion, then, there are two processes that can mask, partly or completely, internal photoemission from metal contacts into antracene. One consists of hole photoexcitation out of surface traps. The experimental investigation of this process constitutes the main topic of this paper. The other process is carrier injection from the contact under study. We feel that in none of the investigations reported on photoemission into anthracene was sufficient attention devoted to an assessment of these two processes, much less to attempts of minimizing their contribution. We maintain that before any photoemission studies are undertaken, one should first check surface (and bulk) photoexcitation using blocking contacts. Conducting glass electrodes are recommended, water contacts being hazardous. Various surface treatments (such as benzene etching) should be tried with the goal of suppressing surface photocurrents. Secondly, one has to ensure that the contact to be studied is non-injecting (in the dark). Checking the reverse photocurrent immediately following the application of a forward voltage (while the sample is kept in the dark) may provide the answer but not in all cases.

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