Field-assisted photo-stimulated charge transfer across photoconductor–dielectric liquid interfaces

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Field-assisted photo-stimulated charge transfer across a photoconductor–dielectric liquid interface has been studied by a high sensitivity signal averaging transient measurement technique. The effects of both the temperature and electric field (below 2×10^5 V/cm) have been investigated. Experimental results were analyzed using an interface model developed earlier to describe the charge transfer kinetics. We have found evidence of direct and indirect transfer of charge across the interface and we have identified the controlling parameters for the desorption rate of charge carriers from the interface into the fluid.

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On a étudié le transfert de charge photostimulé et assisté par le champ à travers l'interface entre un photoconducteur et une liquide diélectrique en faisant appel à une technique de grande sensibilité mesurant les phénomènes transitoires par une methode qui établit la moyenne des signaux. On a étudié les effets de la température ainsi que du champ électrique (en bas de 2×10^5 V/cm). On a analysé les résultats expérimentaux en faisant appel à un modèle d'interface qui a été développé antérieurement pour décrire la cinétique de transfert de charge. On a trouvé des preuves de transferts de charges directs et indirects à travers l'interface et on a identifié des paramètres qui contrôlent la vitesse de désorption des transporteurs de charges allant de l'interface vers le fluide.

[Traduit par le journal]

Introduction

The phenomenon of photo-assisted charge transfer across a photoconductor–dielectric liquid interface has been studied in this experiment. Evidence of charge transfer from a photoconductor into nonpurified dielectric liquids has been reported earlier (1) for high electric fields, and a phenomenological model was developed to describe this process. The experimentally observed transient current pulse was found to depend primarily on two important parameters; the release rate of charge from surface traps on the photoconductor into the lowest vacant state of a neutral impurity molecule adsorbed on the surface, and the desorption rate of the ions from the interface into the liquid. The electric field dependence of the two rates was examined previously for the range 2×10^5 to 10^6 V/cm. Here we investigated the validity of the charge-transfer model further by measuring the thermal activation energies of the rates, and by extending the measurements to lower electric fields (10^4–10^5 V/cm).

Experimental Approach and Charge Transfer Model

We used a typical capacitor cell arrangement for our experiment. The electrodes were SnO_2 coated glass, overcoated with a thin film of SiO (thickness 1000 Å) to prevent charge injection directly from the electrodes. Metal-free phthalocyanine was vacuum deposited (thickness 1300 Å) onto one of the SiO coated electrodes. The photoconductor was separated from the other electrode by a Teflon spacer, forming a cell which was filled with practical grade decane. The liquid was obtained directly from the supplier's container and was not further purified. The thickness of the liquid was 120 μm and the electrode area was 1 cm^2.

A Xenon flash lamp (3 μs duration), in conjunction with a band-pass filter (400–800 nm), was used to illuminate the cell. The photo-generated current pulse moved through the photoconductor layer in about 10^{-9} s (2), which was shorter than the response time of our instruments (2 μs). The charge then transferred into the liquid. The current in the liquid increased as the charge carriers desorbed from the photoconductor surface, and decreased as carriers began arriving at the other electrode. The peak of the current trace, shown in Fig. 1, corresponds to the average transient time τ for carriers to move through the liquid. A typical
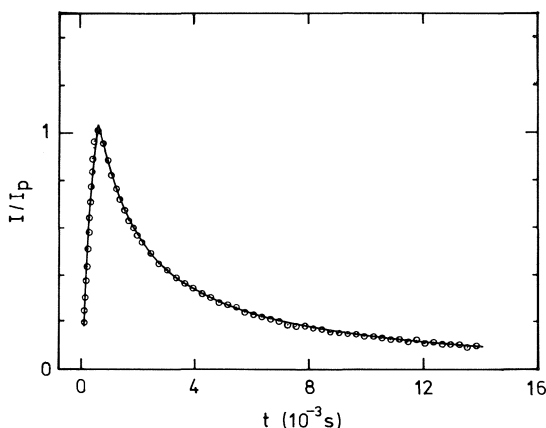
FIG. 1. The least squares fit (solid line) of the single surface trap interface model to a typical transient current pulse (circles) for negative charge transfer from phthalocyanine into decane. The current is normalized by the peak current I_p at $t = \tau$.

value of τ was 10^{-3} s. In terms of the drift mobility μ of the charge carrier, we have

[1] $$\tau = d/\mu E$$

where d is the fluid thickness and E is the electric field in the liquid. The magnitude of the carrier mobility as determined from [1] was of the order of 10^{-4} cm^2 V^{-1} s^{-1}, indicating that the carriers were ions (3).

As mentioned earlier, we restricted ourselves to the low field region between 4×10^4 and 2×10^5 V/cm. The signal in this field range was always below the noise level and the conventional single transient measurement technique was found to be inadequate for this case. We circumvented this problem by using a signal averaging technique. Each of our data points represents the average of a few hundred to a few thousand current traces taken at the same temperature and field. By using this technique, the signal-to-noise ratio is improved by a factor $\sqrt{n}$, where n is the number of current traces averaged. As a check, the average transit time obtained by this technique was plotted as a function of $1/E$, and good agreement with [1] was found.

The temperature in the cell was monitored by a micro-temperature sensor embedded in the dielectric liquid. The temperature was varied from 0 to 100°C and was stabilized to better than ±1°C. At 100°C the sublimed phthalocyanine started to separate from the glass substrate, and the data points obtained at this temperature have only a qualitative significance.

According to the phenomenological model, the transfer of charge from the photoconductor into the liquid requires the presence of an unoccupied state whose energy (relative to the vacuum level) lies below the conduction band energy of the photoconductor. This state can be conveniently supplied by the lowest vacant state of an impurity molecule adsorbed on the photoconductor surface. Direct transfer into the liquid is unlikely because the energy level of the extended electronic state is a fraction of a volt (4), and is well above the conduction band energy of the photoconductor (3.2 eV). As shown in Fig. 2, charge in the photoconductor can either transfer to a neutral molecule directly or via surface traps at a release rate r_2. In the process of desorbing from the photoconductor, the ionized impurity molecule must overcome the potential barrier resulting from the image potential and the applied electric field in the liquid, i.e.

[2] $$U(x) = -\frac{\alpha e}{x} - eEx \qquad \text{for } x \geq a$$

where a has the dimension of the ion radius, e is the electronic charge, and $\alpha = (3/16\pi\varepsilon_f)(\varepsilon_p - \varepsilon_f)/(\varepsilon_p + \varepsilon_f)$, where ε_p and ε_f are the dielectric constants of the photoconductor and fluid, respectively. The position and magnitude of the potential barrier can be evaluated from [2] for different fields.
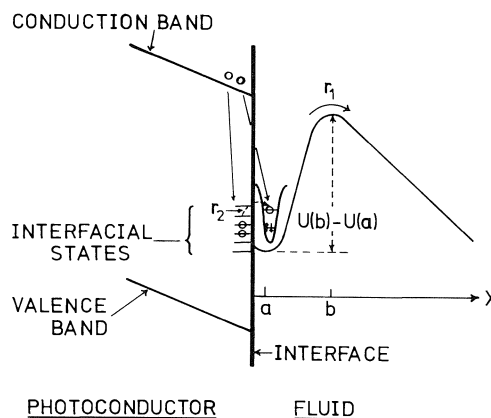

FIG. 2. Schematic of the kinetics of charge transfer from the photoconductor into the fluid. Energy levels of electrons are shown to the left of the interface and the potential well of the ionized impurity molecule in the fluid is shown to the right of the interface. r_1 is the desorption rate of ions from the interface into the liquid and r_2 is the release rate of charge from surface traps into the lowest unoccupied energy level of the molecule adsorbed onto the photoconductor surface.

The expression for the transient current pulse in the liquid has been shown to have the following form (1),

$$[3] \quad I(t) = \begin{cases} i(t) & t < \tau \\ i(t) - i(t - \tau) & t > \tau \end{cases}$$

where

$$[4] \quad i(t) = A[1 - \exp(-r_1 t)]$$
$$+ B[1 - \exp(-r_2 t)] + \frac{Br_2}{r_1 - r_2}$$
$$\times [\exp(-r_1 t) - \exp(-r_2 t)]$$

Expressions for the constants A and B are given in ref. 1, and are not used in the present investigation. The desorption rate of carriers into the fluid is r_1, and r_2 is the release rate from surface traps. The functional dependence of r_1 on electric field and temperature is given by (1),

$$[5] \quad r_1 = CE^{3/4} \exp(-U_t/k_B T)$$

where C is a constant, k_B is Boltzmann's constant, and the total activation energy U_t consists of two parts; the potential barrier height $U(b) - U(a)$ (where $x = b$ corresponds to the potential maximum) and the ion mobility activation energy U_μ, i.e.,

$$[6] \quad U_t = U(b) - U(a) + U_\mu$$

The $E^{3/4}$ part of the prefactor in [5] arises from the change in the curvature at the maximum of the potential barrier as the field is varied.

The temperature and field dependence of the trap release rate r_2 have not been calculated because of lack of information about the physical nature of the surface traps.

Results and Discussion

The charge transfer model was checked by measuring the transient current as a function of the electric field and temperature, and comparing with [3]. The measured current traces were fitted to [3] by a nonlinear least squares computer routine. As mentioned earlier, each current trace used for comparison with the theory represented an average of many traces taken under identical conditions of electric field and temperature. Thus, the relative error of the data points depends primarily on the number of traces used for averaging, and is typically below 5% for most of our traces. The uncertainty in the temperature is less than ±0.5%, and the uncertainty in the value of the electric field is ±2%. Figure 1 shows an averaged current trace
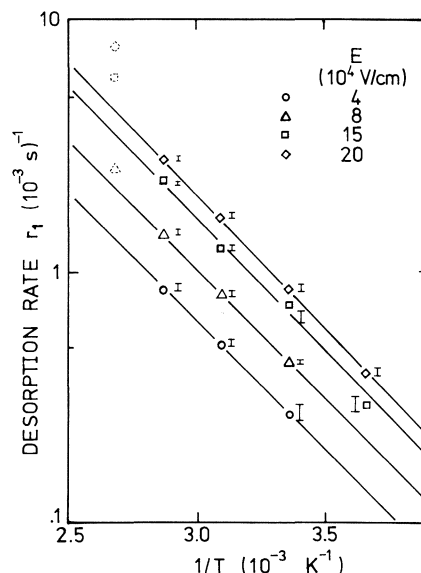

FIG. 3. Temperature dependence of the desorption rate r_1 for four different fields. The slopes at each field are almost identical and give a total activation energy of 0.21 ± 0.01 eV. Data points at 100°C are not very reliable because the photoconductor had partially separated from the substrate.

and the computer fit to [3]. It is evident that [3] describes the shape of the current pulse quite well.

In Fig. 3 the logarithm of the desorption rate r_1 is plotted as an inverse function of temperature for four different electric fields. It should be noted that all data points for the same field lie on a straight line and the lines for the different fields are nearly parallel to one another. This implies that the desorption process of charge carriers is thermally activated, as described by the Boltzmann factor in [5], and the activation energy U_t is not very sensitive to the electric field for the low field range. The rate r_1 is shown in Fig. 4 as a function of the electric field. The data points for the different temperatures all follow the power law $E^{3/4}$ which is shown by the solid lines. This again indicates that the contribution to the field dependence of r_1 from the exponent in [5] is negligible. The experimental value of U_t, as deduced from the slope of the straight lines in Fig. 3, is 0.21 ± 0.01 eV. U_μ can be obtained from the temperature dependence of the charge carrier mobility, shown in Fig. 5. The slope of this line gives an activation energy of 0.17 ± 0.01 eV. The potential barrier height, $U(b) - U(a)$, is thus determined to be 0.04 ± 0.02 eV, with no measured field depen-
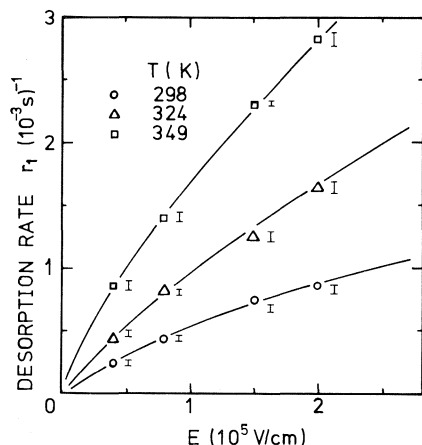
FIG. 4. Electric field dependence of the desorption rate r_1 for three different temperatures. The solid line is a fit to the theoretical expression given by [5].

dence. The value of $U(b)$ estimated from [2] for $E = 2 \times 10^5$ V/cm is about -0.02 eV, which cannot be resolved in our experiment. The barrier height is probably dominated by the ion binding energy at the interface, $U(a)$.

The trap release rate r_2 is plotted as an inverse function of temperature in Fig. 6. As one would expect, the detrapping of charge increases with increasing temperature. Unfortunately, the data for r_2 cannot distinguish whether the charge is released from surface traps or from bulk traps
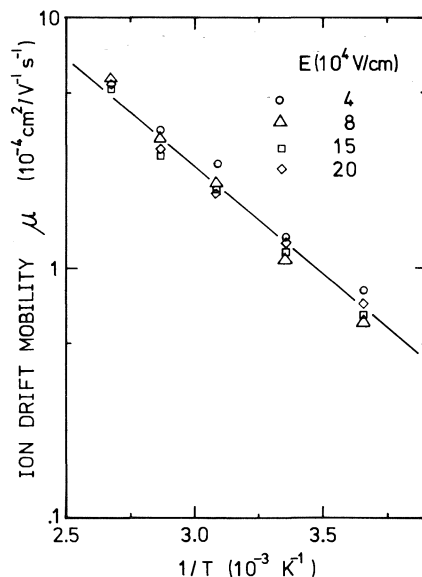

FIG. 5. Temperature dependence of ion mobility for four different fields. The mobility activation energy obtained from the slope is 0.17 ± 0.01 eV.
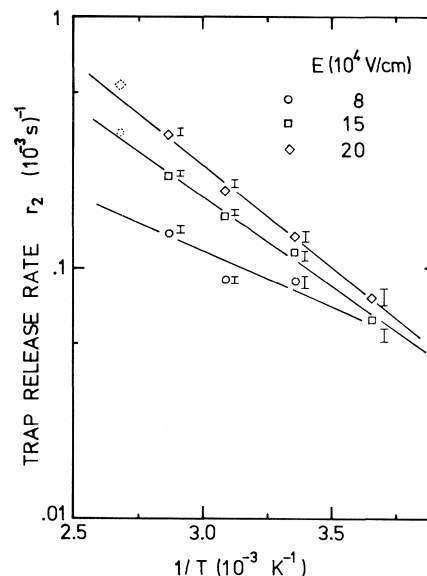

FIG. 6. Temperature dependence of the trap release rate r_2 for three different electric fields.

near the surface. However, we have observed that the charge transfer from different phthalocyanine thin films gives different values of r_2 for identical values of temperature and field. The reason for this variation could be that slightly different film evaporation conditions may result in different surface morphology and different surface states. A more precise control on the vacuum deposition conditions is required to study this effect. For consistency, all measurements presented here were performed on one sample. The field dependence of r_2 shown in Fig. 6 cannot be interpreted at this time because of insufficient knowledge about the physical nature of the traps.

Finally, the effective radius of the charge carrier, a, was determined by two different methods. The value calculated from [2], using the value of $U(a)$ estimated earlier from the activation energy of r_1, is $a \simeq 8$ Å. The corresponding value from Stokes' law, $\mu = e/6\pi\eta a$, where μ is obtained from the transit time data and $\eta = 0.88$ cp for decane at 25°C is $a \simeq 7.4$ Å. The agreement between these two methods of determining a indicates that the small value of the binding energy at the interface is indeed due to the large effective radius of the charge carrier.

In conclusion, we summarize our findings as follows: the phenomenological model proposed earlier (1) gives a good description of the transfer

of photogenerated charge from a photoconductor into a dielectric fluid under an applied electric field. The charge carriers in the fluid are ions, as indicated by the small value of the observed mobility, and charge transfer requires the presence of an impurity molecule with its lowest vacant energy level lower than the conduction band energy of the photoconductor. Both the desorption r_1 of ions from the interface and the release rate r_2 from surface traps are thermally activated. The rate r_1 has a power law field dependence which arises from the effect of the applied field on the curvature of the image potential barrier near its maximum. The variation of the height of the potential barrier with field is very small and is not observed for the low field range investigated. The origin of the field dependence of r_2 is not understood at present. An investigation of the effect of various impurity molecules on the charge transfer is presently in progress.

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Discussion

A. C. Albrecht: We very much appreciate the nice analysis you have presented for the transfer of charge at a semiconductor–fluid interface. We have studied this very system with chlorophyll acting as the semiconducting film and see both the fast and the slow signal. Your model should be very useful in analyzing these results too. An interesting qualitative effect we have seen is that as we add chlorophyll monomer to the fluid phase the slow signal is greatly enhanced. Chlorophyll seems to mediate the discharge at the interface. The actual charge carrier in the fluid phase, though, is very likely a smaller molecule according to mobility estimates.

J. Noolandi: We would be very interested in applying the analysis to your experiment.

This article has been cited by:

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