The Utilization of Time-resolved Dielectric Loss to probe the Role of the Surface in Heterogeneous Photochemistry

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The measurement of time-resolved (or transient) dielectric loss in semi-conductors using an e.p.r. spectrometer interfaced to a flash-photolysis system is discussed. In particular, it is demonstrated that aqueous dispersions of pigments can readily be studied using this technique. In this way, the system can be monitored in the presence of donors and acceptors where dynamic interfacial redox reactions are occurring. A flow system was utilized to avoid setting problems as well as providing the potential for the acquisition of first-flash kinetic data. Finally, surface modified pigments are contrasted to their corresponding starting materials.

Over the past several years we have utilized the technique of flash photolysis/electron paramagnetic resonance (f.p./e.p.r.)[1] to study the kinetics of light-induced free radicals in homogeneous and heterogeneous systems. For example, we have shown that f.p./e.p.r. can follow the light-induced generation and decay of trapped electrons and holes in dispersions of various polymorphs of metal-free phthalocyanine, H_2Pc.[2, 3] We have also found emissive e.p.r. signals in sublimed films of H_2Pc,[4] behaviour which results from chemically induced dynamic electron polarization (CIDEP)[5] arising from a triplet excited-state[6] precursor.

An effort was then made to extend the technique of f.p./e.p.r. to inorganic pigments. This was in part due to the fact that we have been interested in determining the effect of surface modification of inorganic pigments[7, 8] on both charge carrier generation and interfacial change-transfer efficiencies. These results are important in both electrophotography[9] and solar-energy conversion.[10–13] However, the normal f.p./e.p.r. experiments were essentially precluded owing to large changes in the dielectric loss which accompanied each flash.† It was therefore decided to exploit these transient dielectric loss (t.d.l.) signals to provide information on the time dependence of photogenerated charge carriers in these inorganic pigments. This paper presents a preliminary qualitative description of the behaviour of the t.d.l. signals and illustrates some areas in which this phenomenon may be of use in elucidating the kinetics and mechanism of electron–hole pair formation and decay.

† Microwaves are concentrated in the e.p.r. cavity in a mode where the E_1 and H_1 components of the electromagnetic radiation are spatially resolved. In the normal e.p.r. experiment the sample is placed mainly in the H_1 field since it is this field which interacts with the magnetic dipoles. However, samples do extend into the E_1 field, and in cases where light also creates species which interact with the E_1 field, the reduction in cavity Q will be a composite of both magnetic and electric effects. With inorganic, semiconducting pigments the light induced dielectric loss was of such a magnitude that it completely dominated the absorption of microwaves.

Dielectric Loss

The light-induced generation of new holes and electrons will, in most solids, result in changes in the dielectric constant of the solid. If the solid is located in a microwave cavity, there will be a resultant change in the dielectric-loss characteristics of the material and a change in the intensity of microwaves reflected from the cavity.

The utilization of microwaves to probe changes in the dielectric properties of semiconductive pigments under illumination is not new. For example, experiments using steady-state illumination have been carried out (1) on CdS by Hartwig and Hinds,[14] (2) on CdS and ZnS by Kramer *et al.*[15] and Kalikstein *et al.*[16] and (3) on silver halides by Kellogg *et al.*[17] Time resolved experiments using pulsed light sources have been carried out on CdS, ZnS, silver halides, TiO_2, ZnO and Se. Collier *et al.*[18] used a pulsed light source to observe transients in CdS and copper-doped CdS powders dispersed in an insulative organic binder. They suggested that the rate of decay of the transient was determined by the rate of release of electrons from surface traps. Klosterboer *et al.*[19] and Dierssen and Sahyun[20] have also used this method with CdS and Cd(S, Se) powders.

Kellogg[21] was the first to use this method to measure photoelectron lifetimes in silver halides. This was followed by (1) Beutel's[22] work on cubic AgBr emulsions, (2) Spoonhower's[23] photoconductive and photodielectric measurements on silver halides, (3) the e.p.r. and microwave study of Eachus and Spoonhower[24] on the influence of Pb^{2+} ions on the photochemistry of AgCl and finally (4) the modification of ionic conductivity as monitored by dielectric loss in silver halides by Chen *et al.*[25]

This same technique can be utilized to measure changes which occur in the dipole moment of a molecule upon absorption of a photon. This has been demonstrated by Fessenden *et al.*[26, 27] and Warman *et al.*[28–31] In addition electrochemical reactions have been monitored by changes in the dielectric loss using ZnO in both aqueous[32] and non-aqueous[33] media. Bogomolni *et al.*[32] also observed similar changes upon direct photoexcitation of ZnO.

Two recent reports have demonstrated that a time resolution of *ca.* 5 ns using this technique can be achieved. Warman *et al.*[34] have studied TiO_2, CdS and CdSe powders dispersed in non-polar liquids with sufficient sensitivity to obtain kinetic traces after a single flash of light. Deri and Spoonhower[35] have matched this time resolution as well as obtaining single-flash kinetic data in silver bromide emulsions.

Apart from the single crystal ZnO/H_2O system of Bogomolni *et al.* and very recent work by Sahyun,[36] in which the effects of both aqueous and polar solvents on the transient dielectric loss signal were observed by allowing the CdS dispersion to flow down the side of a 3 mm quartz tube, there has been little success with the use of H_2O as a dispersant. In this report we present a technique of using normal e.p.r. equipment to study readily aqueous (or non-aqueous) dispersions under flow conditions with the equivalent achievement of single-flash kinetics data. This study of aqueous dispersions is important since one can then monitor the t.d.l. signals in dispersions containing donors and acceptors. *I.e.* the lifetimes of the charge carriers can be monitored in systems where a high efficiency of interfacial charge transfer is operative. The report also details our initial efforts at using the technique to monitor charge-carrier lifetimes in powders and polymer bound powders. Certain photoactive pigments were also contrasted with their surface-modified derivatives (platinized CdS and phthalocyanized ZnO).

Experimental

A Varian E-12 e.p.r. spectrometer was used to measure the t.d.l. signals. These transient signals were digitized by a Nicolet model 2090 Explorer III digital oscilloscope and subsequently transferred to a Nicolet model 1180 computer for signal-averaging and data analysis. In this type of experiment no external magnetic field was applied, and the

output from the crystal detector, amplified by a Comlinear Corp. CLC100 voltage amplifier, was directly measured (no magnetic field modulation). Most of the experiments used the E-238 e.p.r. optical cavity which operates in the TM_{110} mode with an unloaded Q factor of 12 000. For certain experiments a Varian E-234-2 (TE_{102}) cavity was employed. Microwave power was typically between 0.1 and 10 mW. Saturation was observed with most systems above 10 mW.

The sensitivity of the method was critically dependent on the position of the sample cell within the cavity. The signal could be significantly enhanced by placing the sample near the maximum of the E field. This was possible for thin wafers and powders. However, with aqueous dispersions, the dielectric loss due to water limited the positioning of the cell to within a small deviation from the node of the E field.

Two flash sources were used: a Photochemical Research Associates Nitromite LN-100 nitrogen laser (337 nm, 40 μJ, pulse width *ca.* 0.1 ns) and a PRA 610 C Xe flash system with a flash half-maximum of 1.5–2 μs. A fast-response photodiode was used to trigger data collection of the transient recorder. Accumulated response profiles were collected with the light beam blocked and open, enabling the use of spectrum subtraction techniques to correct for r.f. noise generated during lamp triggering. Typically, 500–2000 scans were performed at a pulse frequency of *ca.* 10 Hz.

The powders were obtained commercially and the surface modified derivatives by the methods previously outlined.[7, 8] Single-crystal silicon was obtained from Wacker. ZnO was embedded in solid PMMA by thermal polymerization of the monomer at 55 °C for 7 days.

Pigment dispersions (13 g per 100 cm³) were prepared in a magnetically stirred reservoir under constant gas flow (O_2, Ar or air) using doubly distilled water. The dispersions were pumped through an aqueous flat cell located in the resonance cavity of the microwave bridge and back into the reservoir by means of a peristaltic pump. Flow rates of *ca.* 6 cm³ min⁻¹ were maintained throughout the duration of the experiment. (The residence time of moving particles within the effective cell dimensions was calculated to be *ca.* 0.5 s.)

Results and Discussion

Solids (Crystals or Powders)

Silicon

A piece of an undoped single crystal of silicon which was attached to an e.p.r. tube gave the t.d.l. signal shown in fig. 1. A very rapid increase in the dielectric loss upon exposure to the flash of light, as well as the rapid return ($\tau_e < 1$ μs) to pre-exposure level, is evident. In fact, this response is instrument limited ($\tau_e = 0.4$ μs). This implies that charge carriers generated by the light are trapped, released and recombine within < 1 μs. A temperature study revealed that the response remains instrument limited (to 80 K). However, crushing the silicon to a coarse powder resulted in a longer-lived tail in the t.d.l. signal. The temperature dependence of the t.d.l. of the crushed silicon (fig. 2) revealed that the decay kinetics decreased (τ_e increased) as the temperature was lowered. These results suggest that crushing creates new surface states which can effectively trap photoinduced charge carriers. These charges must be released (which will be a function of the temperature) before they can recombine.

Cadmium Sulphide

The t.d.l. signal from CdS is shown in fig. 3. These data follow a first-order decay (except for the initial few points) with a τ_e (reciprocal of the slope of ln (intensity) *vs. t*) of *ca.* 13 μs (fig. 4). The initial deviation is typical of CdS,[18, 19] although reported values of τ_e
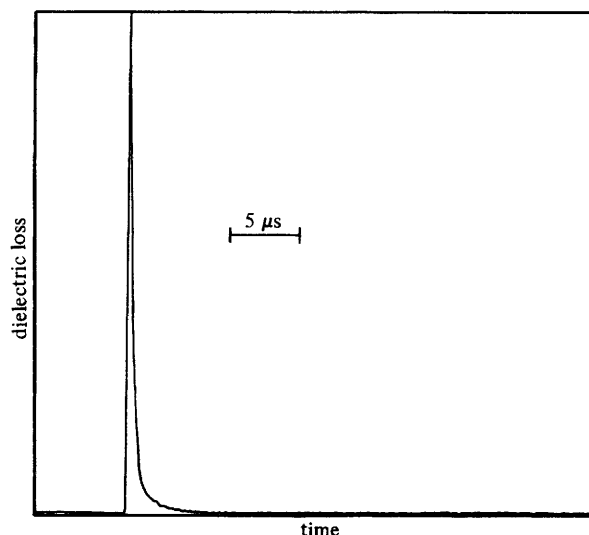
Fig. 1. The t.d.l. signal of intrinsic Si upon exposure to the nitrogen laser ($\lambda = 337$ nm).
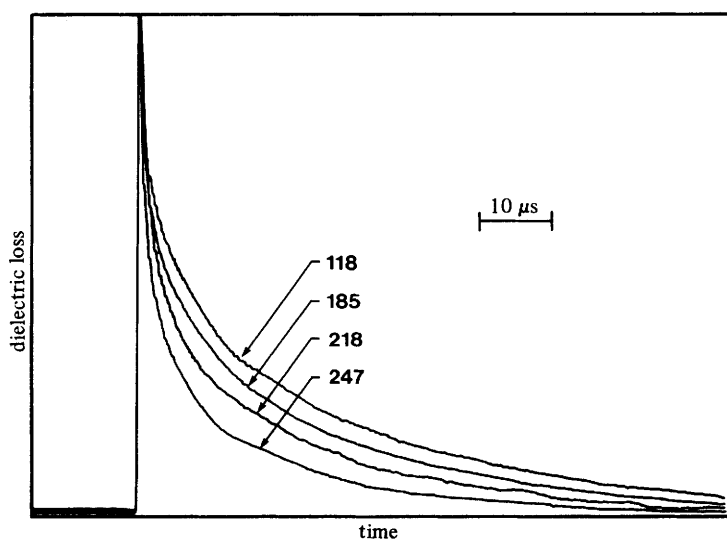

Fig. 2. The temperature dependence (in K) of the t.d.l. signal from an Si wafer which had been crushed.

range from 1 to 88 ms.[18, 19] These longer lifetimes may result from the fact that the particles were embedded in an insulating polymer binder. (We will demonstrate below with ZnO that a polymer binder can have a profound effect on decay kinetics.) Single crystal CdS had a slightly larger half-life of 18 μs. This first-order behaviour has been accounted for by postulating the thermal release of relatively shallow trapped conduction electrons which then encounter a recombination centre.[18]

When platinized CdS[7] was examined, the lifetime was significantly increased, ($\tau_e \approx 500$ ms) (fig. 5). This result demonstrates the critical importance of the state of the
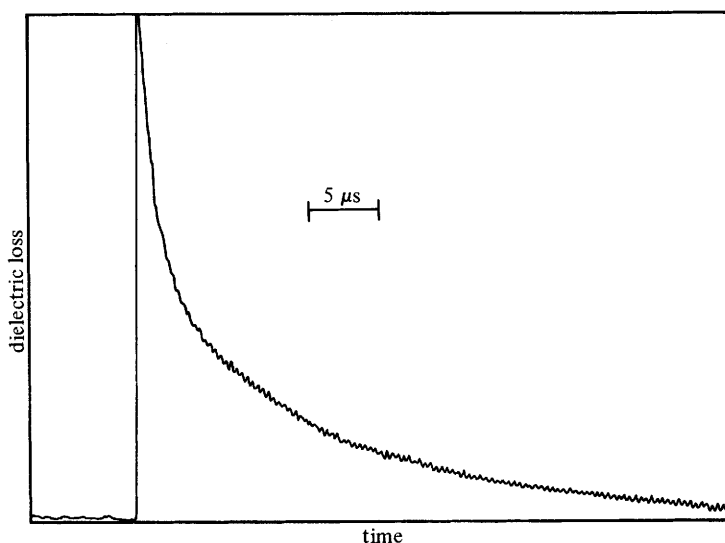
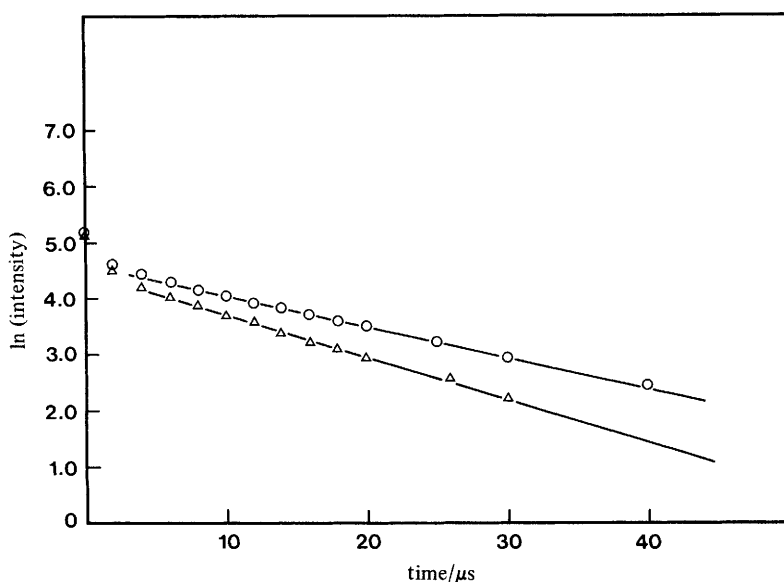**Fig. 3.** The t.d.l. signal from CdS powder using a nitrogen laser.

Fig. 4. Plot of ln (intensity) *vs.* time for both CdS powder and single crystal. The lifetimes given are the reciprocals of the slopes: $\bigcirc$, crystal ($\tau = 18\ \mu$s); $\triangle$, powder ($\tau = 13\ \mu$s).

surface in controlling the lifetime obtained from t.d.l. signals. In this case the CdS has Pt^0 clusters of *ca.* 30 Å diameter homogeneously distributed on the surface. This platinization greatly affects the photochemistry of CdS dispersions by increasing O_2 reduction by an order of magnitude, and in the absence of O_2 and in the presence of EDTA allowing the evolution of H_2 gas.[7]
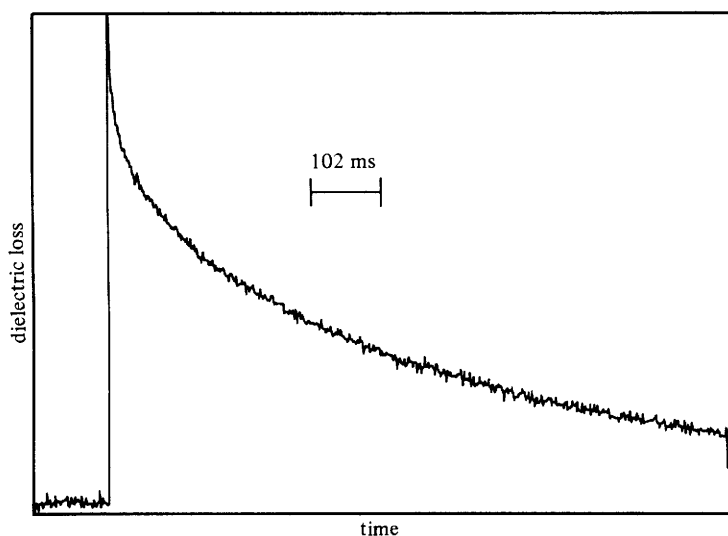
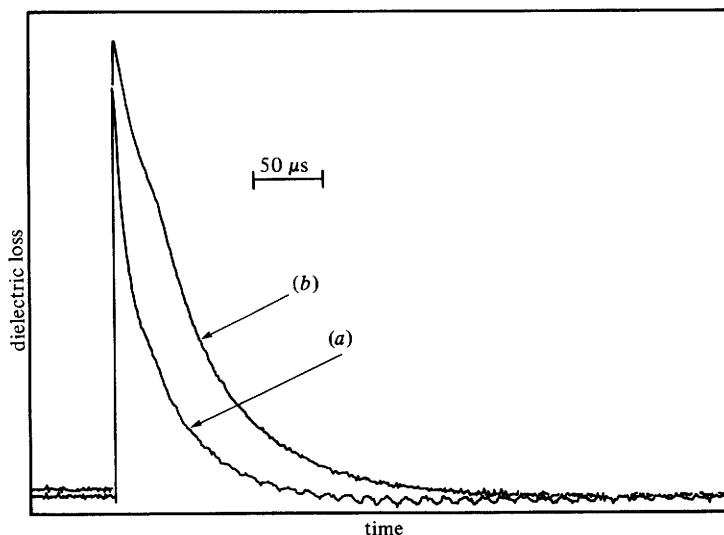**Fig. 5.** The t.d.l. signal obtained after platinization of CdS ($\tau = 500$ ms).

Fig. 6. The t.d.l. signals of a ZnO/ZnPc powder with excitation at (*a*) 375 nm and (*b*) > 620 nm using a PRA 610C flash lamp. The shoulder in the 620 nm generated signal is due to an afterglow at 25–30 μs with this flash lamp.

Zinc oxide

ZnO powders gave t.d.l. signals which were first-order in their decay (again neglecting the first few data points) with $\tau_e = 22$ μs. The action spectrum for these pigment particles coincides directly with the absorption spectrum of ZnO. [*I.e.* only light which can induce a band transition ($\lambda < 390$ nm) gives rise to a t.d.l. signal.] When the ZnO particles were dispersed in freshly distilled methyl methacrylate, which was subsequently heated to induce polymerization, there was surprisingly no t.d.l. signal on exposure. Evidently, this

method of incorporation of ZnO into an insulative polymer binder must either create deep surface states and/or remove the shallow states which give rise to t.d.l. signals. Again, the extreme importance of the state of the interface is evident.

Another surface-modified pigment which was used in this study was phthalocyanized ZnO.[8] This pigment consists of a core of ZnO with a covering of 1 or 2 monolayers of ZnPc. As with normal ZnO powder, direct bandgap excitation resulted in a t.d.l. with $\tau_e \approx 25~\mu s$ (fig. 6). However, illumination with red light (absorbed by the ZnPc) also resulted in a t.d.l. signal but with $\tau_e = 56~\mu s$ (fig. 6). It has been previously shown with e.p.r. detection that steady-state excitation of the phthalocyanized ZnO with red light leads to a $g = 1.096$ signal characteristic of trapped conduction electrons in ZnO.[37] Hence a photoinduced electron transfer from ZnPc to ZnO can occur. With the present system this transfer is also detected but in a transient mode. Recombination takes longer if the electron donation arises from the surface resident ZnPc (*i.e.* 56 *vs.* 25 μs).

Metal-free Phthalocyanine

Metal-free phthalocyanines did not give rise to t.d.l. signals upon flash exposure. This was not unexpected, since previous work using H_2Pc with f.p./e.p.r. was successful.[2–4] It is important to note that mobilities in phthalocyanine[38] are typically 0.1 cm^2 s^{-1} V^{-1}, a value which is *ca.* 3 orders of magnitude less than mobilities for these inorganic pigments. This implies that the loss observed (dP_{ABS}) is dependent on both the number of charge carriers and the mobility:[39]

$$dP_{ABS} \simeq V_S e\mu E_S^2 \, dn \tag{1}$$

Here E_S is the microwave electric field at the sample, V_S is the sample volume, μ is the carrier mobility, e is the electronic charge and dn is the number density of photocarriers.

Dispersions

It is important to determine the lifetimes of charge carriers under conditions where interfacial electron transfer reactions can occur. This is often the case in aqueous dispersions, where added donors and acceptors can undergo redox reactions with the photogenerated holes and electrons. However, two difficulties are encountered: (1) the large dielectric loss with H_2O and (2) the rapid settling of the high density particles in H_2O. These difficulties were overcome by using a e.p.r. aqueous flat cell coupled to a closed-flow system. Aqueous ZnO dispersions were pumped through the flat cell at a rate of 6 cm^3 min^{-1}. The t.d.l. signal again showed first-order decay kinetics with $\tau_e = 36~\mu s$. Since this was a closed system the system could be bubbled with either O_2 or argon prior to flow conditions. Results from these experiments revealed that no real difference was observed in τ_e for the O_2 or argon bubbled systems.

It is known that sodium formate (0.1 mol dm^{-3}) is an extremely effective donor for the ZnO-sensitized photochemical generation of H_2O_2.[40] In fact, the quantum efficiency of electron reduction of O_2 is close to unity.[41] The formate anion is oxidized to the CO_2^- radical. When sodium formate at 0.1 mol dm^{-3} was added to the dispersion, the value of τ_e obtained from the first-order kinetic decay was *ca.* 60 μs, *i.e.* nearly twice as long as the formate-free case. This result can be interpreted as hole annihilation by the formate freeing the electrons from hole–electron recombination and thereby increasing the lifetime of the electrons. These electrons must ultimately reduce O_2, and since the lifetime of the shallow trapped electrons is *ca.* 60 μs, the interfacial electron-transfer process must occur in a time > 60 μs. This assumes that the t.d.l. signal is in fact representative of the fate of all the photogenerated electrons.

Surfactants can adsorb onto ZnO from solution and could affect the observed τ_e t.d.l. lifetime. As a consequence, Aerosol-OT, Triton X-100 or poly(vinyl alcohol) were added

to these ZnO aqueous dispersions. The lifetimes determined from the t.d.l. were 29, 43 and 47 μs, respectively. Addition of 0.1 mol dm^{-3} NaCl had no effect on the observed lifetime.

Conclusions

It has been demonstrated that a conventional e.p.r. system in conjunction with a flash-photolysis system can effectively monitor transient changes in the dielectric loss (microwave absorption). The system is ideally suited for aqueous dispersions using an aqueous cell with or without flow conditions. This is important, owing to the large interest in interfacial redox reactions in aqueous medium. With the flow system, the equivalent of first-flash data can be achieved.

This technique can be used to study the effect of surface modification and interfacial environment in general on the lifetimes of generated charge carriers. These lifetimes can also be monitored under conditions of interfacial charge transfer, and therefore the technique provides a probe for the study of the kinetics of heterogeneous electron-transfer reactions. It will be important however to quantify the t.d.l. technique (*i.e.* the number of electrons giving rise to a certain signal) in order to determine the significance of the results.

The state of the interface controls the observed lifetimes and suggests that the charge carriers (electrons in these cases) have found shallow traps very near the surface.

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