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Studies on the Synergism of Cyanine Dyes Used in Photography*

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ABSTRACT

Supersensitizing combinations of cyanine dyes adsorbed on a p-type Si single crystal were studied by measurements of the Dember effect; the interaction between dyes was confirmed. The addition of supersensitizer increases the capability of hole-trapping, regardless of whether it is exposed to light or not.

1 INTRODUCTION

Synergism, i.e. the observable or measurable enhancement of the effect of a combination of substances compared with that of the same amount of individual components, is often encountered in organic textile dyes, pigments and photographic sensitizers. The mechanism of the synergistic effect has been widely studied and it has been observed that the chemical

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structures of two compounds having synergism are very similar to each other. It can be reasonably considered that synergism results from intermolecular interaction (electron transfer and energy transfer) due to the similarity of electronic energy levels between the molecules.

Supersensitization, i.e. synergism in the photographic process, has been previously investigated[1] and in a previous paper,[2] we concluded that interaction between cyanine dyes plays an important role in the supersensitization. It is well known that a supersensitizing combination of a mesoethyl substituted naphthothiacarbocyanine and an allopolar trinuclear cyanine, is to trap the positive holes of the sensitizer, with the formation of a positive hole of the supersensitizer. Thus the recombination of the photoelectron injected into the conduction band of AgX and the positive hole of the sensitizer is prohibited.[2-4] In this present paper, a p-type silicon single crystal [(111) face], which acts as a 'hole source', is used as the substrate for the systems to be investigated. Supersensitizing combinations of cyanine dyes adsorbed on the Si (p-type) (111) face were studied by measurements of the Dember effect and the results and conclusions obtained are not only relevant to silver halide emulsion systems, but are also of interest in comparison with other types of dyes adsorbed on Si single crystals.

2 EXPERIMENTAL

2.1 Sample preparation

A p-type silicon single crystal doped with boron of about $10^{17}/cm^3$, was cut into pieces of ϕ 25 mm, thickness 0·5 mm. The exposure face was the (111) face. The gap band width was 1·08 eV (300 K) for intrinsic single crystals, in which the diffusion coefficients were 38 cm^2/s and 13 cm^2/s for electrons and holes respectively.

A piece of the p-type Si single crystal was placed into a methanol solution of the cyanine dye. Only one face of the single crystal adsorbs the dyes. The chemical structures of the dyes studied are shown in Fig. 1.

2.2 Dember effect measurements

A block diagram of the measuring circuit for the Dember effect is given in Ref. 5. The light source used in the experiments consists of a specially shielded Xenon 437A Nanopulser, which gives a uniform, noise-free exposure of 0·02 $\mu j/cm^2$ on the sample plane. The sample cell, amplifier and the scope were identical to those used previously.[5]

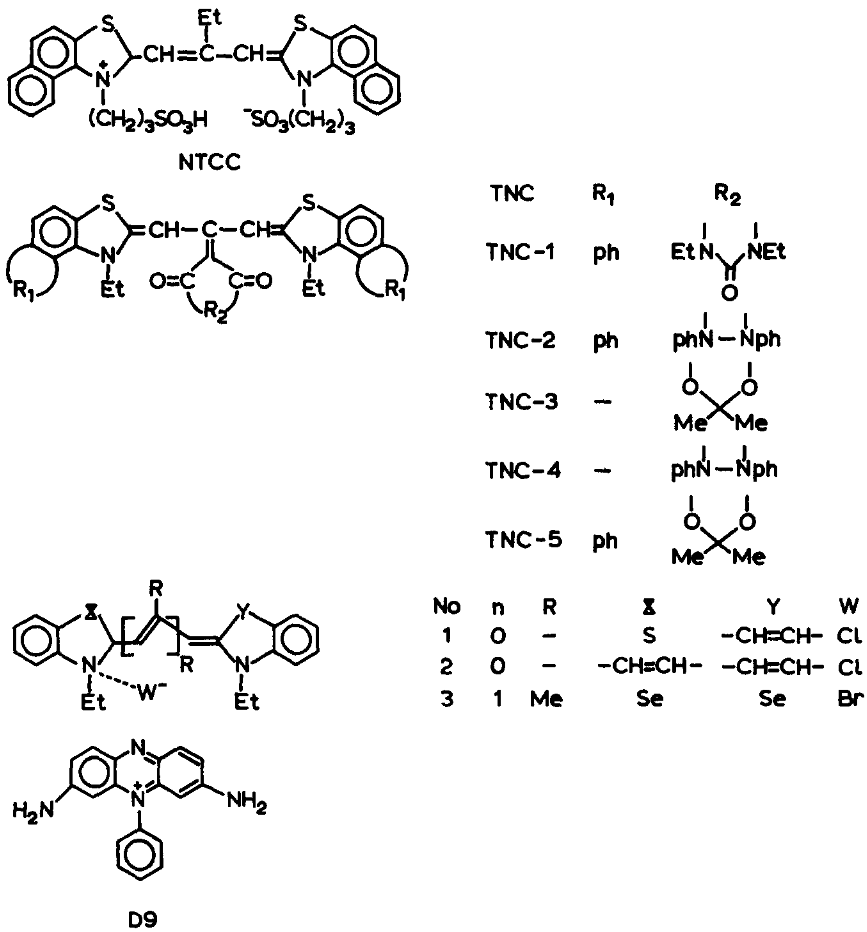

Fig. 1. Chemical structures of dyes studied in this paper.

3 RESULTS AND DISCUSSION

3.1 Silicon single crystal

The Dember photovoltage of the p-type silicon single crystal is shown in Fig. 2.

The dominant charge carrier in a p-type silicon single crystal is the hole. Corresponding to that, there are many electron acceptors in the gap band (between the conduction and valence bands). When excited by light, energy levels of the acceptors can trap electrons, so the lifetime of the photoelectron becomes shorter. The photovoltage (positive) decays rapidly after passing through a maximum point. On the other hand, the lifetime of holes (dominant carrier) is longer. The holes migrate continuously in the direction

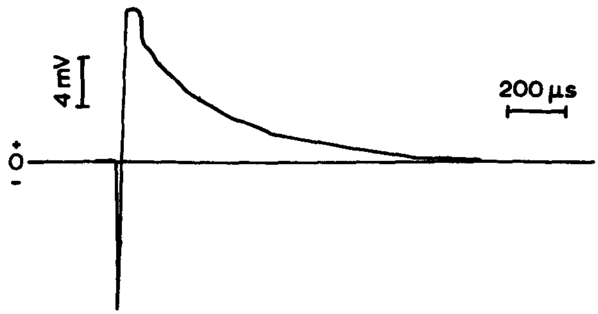

Fig. 2. Photovoltage of p-type silicon single crystal.

of the trapped photoelectrons and the sign of the signal becomes negative over a period of time. Since the amount of photoelectrons is small in the p-type semiconductor, the recombination of holes with electrons has only a small possibility and therefore the decay of the negative signal is slow (as seen in Fig. 2). Because the p-type silicon is not as sensitive to light as silver halides, the results are reproducible, with a relative error less than 5%.

3.2 NTCC/TNC systems adsorbed on Si (p-type)

The cyanine dyes (or dye combination) are absorbed only on one face of the silicon; exposure of the other face, the Dember photo voltage was measured. The results are shown in Figs 3 and 4.

Since the dyes were not exposed to the light, and the Si is intransparent, the dyes did not excite in these experiments (Figs 3 and 4). The results obtained are attributed mainly to intermolecular interaction. The influence on the diffusion holes in Si (p-type) is exhibited especially in Figs 3 and 4. The hole trap theory of supersensitization,[6] in which the role of supersensitizer is proposed to promote the ionization of the exciton or to trap the positive hole of the sensitizer, has already been demonstrated in our previous studies.[2] The results obtained in the present paper are important in ascertaining whether or not the substrate Si (p-type) is a 'hole source' and whether or not the supersensitizing combination of dyes trap the hole from

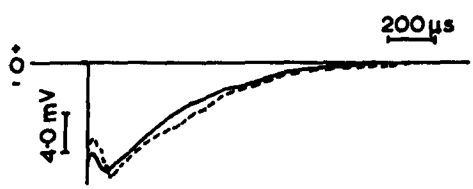

Fig. 3. Dember photovoltages of: (⋯⋯) Si/NTCC + TNC-3); (——) Si/NTCC + TNC-4 with Si facing light.

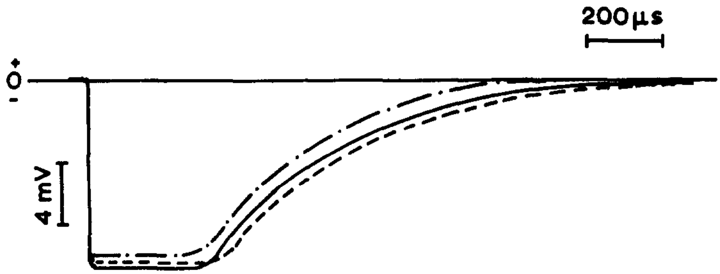

Fig. 4. The photovoltages of: (——) Si/NTCC + TNC-2; (– – – –) Si/NTC + TNC-5; and (–·–·–·–) Si/NTCC, with Si facing light.

the Si, as in the case of the AgX system. The answer is demonstrated in Figs 3 and 4. The NTCC/TNC dye combination will trap the positive holes which are formed in the Si (p-type). Therefore, the recombination of the holes is much slower, and the diffusion of holes in the direction to the exposed face is partly prohibited. Sign reversal does not appear in the measurements. The negative component, under the conditions of the experimental arrangement, was attributed mainly to the slow diffusion of holes. The diffusion behaviour of charge carriers is demonstrated in Fig. 5.

For a p-type silicon single crystal (Fig. 2), because the holes were not trapped, sign reversal of the signal appeared, due to the diffusion of holes towards the exposed face. In comparison, while the reverse side of Si adsorbed the dyes, interaction between dyes would result in the trap of holes from the Si phase, as seen in Figs 3 and 4. The trap of holes also appears for NTCC alone. However, the capability of hole-trapping increases with the addition of supersensitizer TNC and the decay of the negative signal is slow for supersensitizing systems.

The capability of hole-trapping is different for different supersensitizers, which can be demonstrated by supersensitization in a AgX emulsion. It was

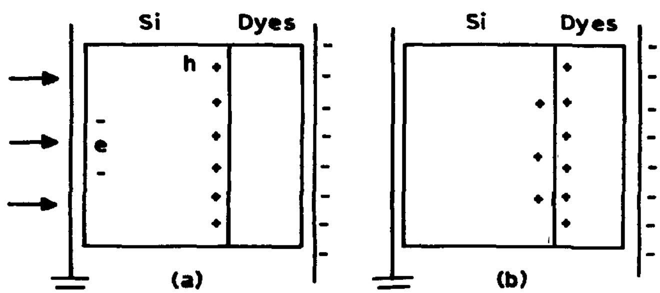

Fig. 5. Diffusion of charge carriers: (a) initial period; (b) after a period of time (holes are tied to the dyes).

found in our previous work[7] that some holopolar trinuclear cyanine dyes (e.g. TNC-2, TNC-5) can supersensitize NTCC very well. The increasing value of photographic sensitivity (ΔS) was about 3·5 Din. However, ΔS for TNC-3 or TNC-4 combined with NTCC was only about 1·0 Din. The difference might result from the fact that the basicities of the heterocyclic rings of TNC-3 and TNC-4 are lower than those of TNC-2 and TNC-5, i.e. a lone electron pair on the N atoms of the heterocyclic ring of TNC-2 and TNC-5 is more readily transferred from the ring to the polymethine chain than in the case of TNC-3 and TNC-4. Thus, one basic nucleus in TNC-3 or TNC-4 is twisted out of plane to form the dimethine merocyanine dye. Thus TNC-3 and TNC-4 are poor supersensitizers. In general, a poor supersensitizer traps holes poorly. Therefore, in the NTCC/TNC systems adsorbed on Si (p-type), this difference becomes apparent (Figs 3 and 4). For TNC-3 or TNC-4, a part of the holes do not trap the dyes, as in TNC-2 or TNC-5 systems. The diffusion of holes towards the exposed face will result in some change of negative signal, as seen in Fig. 3, which shows that the Dember photovoltages of the system can demonstrate the capability of hole-trapping of supersensitizers. The results are consistent with the conclusion in our previous work[2] that the role of supersensitizers can be correlated directly with their measured Dember effects.

The experimental results imply that interaction between dyes in the initial process is to trap holes, regardless of excitation by light or not. In the discussion of latent image formation, Mitchell[7] proposed that, at first, the holes are trapped and recombined after exposure, thus producing an interstitial silver ion, $Ag^{+}i$. It is considered that these interstitial ions do not exist in practical emulsion AgX grains. From our point of view, the action of trapping holes of the supersensitizing combination in the initial process (before light exposure) meets the necessary condition of latent image formation proposed by Mitchell.

3.3 No. 1/No. 2 (No. 3) systems

The experimental results are shown in Figs 6 and 7 for No. 1/No. 2 (or No. 3) systems based on Si (p-type).

The results shown in Fig. 6 are consistent with those for NTCC/TNC systems, especially for trapping of holes by a supersensitizing combination. The addition of supersensitizer increases the capability of the dyes to trap holes and, this results in holes being trapped in the dye layer. The Dember signal obtained thus has a negative sign (Fig. 6(b)) and it is apparent that the role of the supersensitizer is to trap holes.

It can be concluded that the interaction between dyes is very important for synergism (supersensitization in the case of photography) and that the

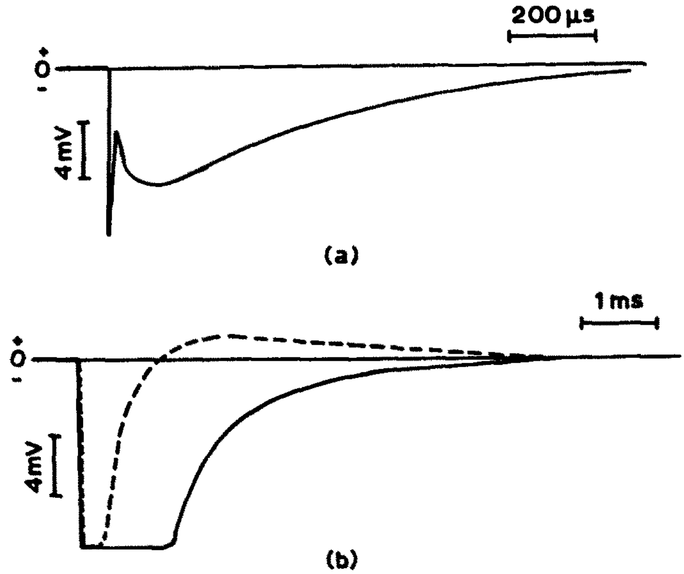

Fig. 6. Dember effect of: (a) Si/No. 1 + No. 2; (b) (———) Si No. 1 + No. 3, (- - - -) Si/No. 3.

interaction takes place in the initial process, regardless of light excitation or not.

In order to confirm this, a desensitizer (Dye 9) was used for similar experiments (Fig. 7) adsorbed on p-type Si single crystal. Since Dye 9 is a densitizer, it traps electrons more easily, thus explaining the results shown in Fig. 7. In contrast to sensitizers, desensitizers have low capability of trapping holes, but trap electrons more easily. Therefore, in the initial stages of exposure, electrons (in spite of their small amount) were tied to the D-9 phase near the interface of Si/D-9. This results in the appearance of a positive Dember signal. After passing through a maximum, holes then migrate in the

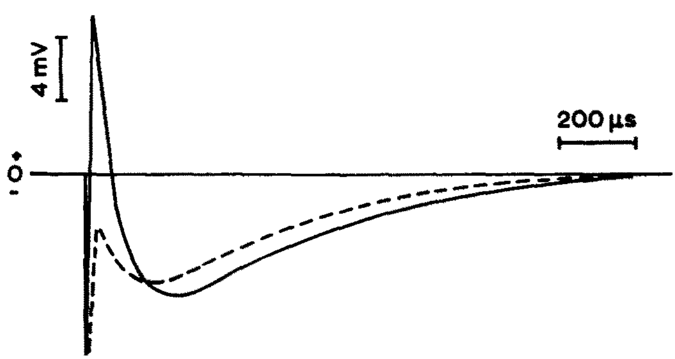

Fig. 7. The Dember Photovoltage of D-9 adsorbed on Si (———) with and (- - - -) without No. 1 dye, for Si facing light.

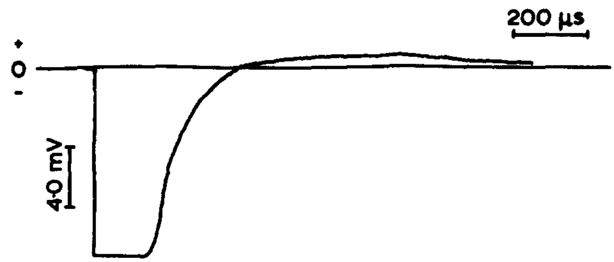

Fig. 8. The Dember photovoltages of D9/Si with D9 facing light.

direction of tied electrons and recombine with electrons. Sign reversal appears, which is attributed to the slow diffusion of holes. Where supersensitizer No. 1 is added, the interaction between dyes increases the capability of trapping holes. Thus the formation of supersensitizer positive hole (No. 1) dominates for the D-9/No. 1 system. This case is similar to that of the NTCC/TNC-3 and NTCC/TNC-4 systems, since the combination between D-9 and No. 1 is well known as a poor supersensitizing system. Compared with that, it can be deduced that NTCC/TNC-3 and NTCC/TNC-4 are not good combinations for supersensitization. Data for the sensitivity of the real emulsion confirms that NTCC/TNC-3 (or TNC-4) is not a good supersensitizing system. In fact, there are many electron acceptors in the desensitizer. D-9 could be considered as a p-type material relative to the sensitizer and therefore the holes, when D-9 is exposed, migrate in the direction of the incident light, resulting in a negative signal. The results shown in Fig. 8 are consistent with this conclusion.

4 CONCLUSIONS

The interaction between dyes of a supersensitizing combination has been confirmed by results when the dyes are adsorbed on a p-type Si single crystal. The addition of supersensitizer increases the capability of trapping holes, regardless of excitation by light.

The experiments exhibit the diffusion of holes in the systems—Si (p-type)/dyes. It can be considered that the capability of trapping holes be correlated with their measured Dember effects.

This interaction between dyes is considered as a primary cause of supersensitization, a particular case of synergism used in photography.

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