

Free-Volume Trapping in Charge Generating Layers

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Abstract

The concept of free-volume trapping was first reported for single-layer aggregate (SLA) photoconductors.

More recently, we have studied this phenomenon in multi-active photoconductors with separate charge generation and charge transport layers, CGL and CTL, respectively. We have found that trapping occurs in the CGL at weakly absorbed wavelength. It was proposed that excess free-volume amplified trapping by a dopant at the surface of the charge generating material enhanced recombination of the geminate hole pair, resulting in lower photoregeneration efficiency.

In this work, we have studied the free-volume trapping phenomenon in multi-active photoconductors doped with molecules of various oxidation potentials. These studies have made it possible to isolate free-volume from intrinsic trapping. We have reconfirmed the role of the charge generation layer and the importance of surface and bulk charge generation. Free-volume trapping is dominant at trap depth below 0.2 V. Above that, intrinsic trapping completely dominates at the trap concentration level of the experiment. Lower trap concentration will most likely delay the dominance of intrinsic trapping.

Introduction

The concept of free-volume trapping was first reported for single-layer aggregate (SLA) photoconductors.[1,2] The drying of SLA films, at temperatures above the glass transition temperature T_g of the SLAs amorphous phase, followed by rapid cooling, generates excess free volume. It was proposed that excess free volume in the photoconductor film can act as a physical barrier to transport, amplifying hole range limitations.

More recently, we have studied this phenomenon in multi-active photoconductors with separate charge generation and charge transport layers, CGL and CTL respectively.[3] We have found that trapping occurs in the CGL at a weakly absorbed wavelength. It was proposed that excess free-volume amplified trapping by a dopant at the surface of the generating material enhanced recombination of the geminate hole pair, resulting in lower photogeneration efficiency.

The present study looks at an oxidation potential series of dopants to further elucidate this phenomenon.

Experiments

We used a cylindrical 30 mm aluminum drum. All three layers were dip coated at 0.3 ips, dried at 100 °C for 30 min, and allowed to cool to room temperature in the dark. For aging studies, the coated drums were heated at 110 °C for 30 min in a Blue M oven, and allowed to cool to room temperature in the dark for 1 hour. At that time, the photo-induced discharge curve (PIDC) was measured at two different wavelengths, 690 and 780 nm, using a PDT-1000 test equipment from Quality Control Engineering, Inc.

Results and Discussions

The multi-active photoconductors used in this study are described in Table 1. Charge generation layers 1-5 use a 6-micron aggregate composition similar to the SLA[1] except that a titanyl phthalocyanine pigment is included at 5 wt% to impart infrared sensitivity. CGL-2 to CGL-5 are doped with DAPM, TAA, DEH, and DTP molecules (0.1 mol). All have oxidation potentials lower than that of TTA(0.89 V), or TAPC (0.92 V), except DTP. Thus they are all traps. CGL-1 is undoped. CGL-6 uses a 0.50-micron 50/50 wt/wt% of a polymer/pigment composition. The charge transport layers CTL-2 to CTL-5 use a combination of two transport materials, tri-p-tolylamine, TTA, 1,1-bis (4-p-tolylamino-phenyl) cyclohexane, TAPC, and are respectively doped with DAPM, TAA, DEH, and DTP. CTL-1 is undoped.

Trapping at Weakly Absorbed Wavelength

The effect of incubation and aging on the sensitivity of the undoped multi-active photoconductor, OPC-1, using 5 wt% pigment is shown in Figure 1. At the weakly absorbed 780 nm, very little trapping occurs, with complete recovery after about 25 days. With no trap available in neither the CGL nor the CTL, this result is fully expected. On the other hand, the DAPM-doped OPC-2 exhibits a relatively large free-volume trapping (Figure 2). Equilibrium photodischarge is obtained after 25 days at the exact time where complete recovery occurred for the undoped OPC-1. However, the DAPM-doped OPC-2 never reached the performance of OPC-1 even after 78 days. We believe this is due to intrinsic trapping, mainly in the CTL.

We would expect to see the same phenomenon in the TAA and DEH-doped OPC-3 and OPC-4, respectively. The results of Figures 3 and 4 testify to that. Figure 5 shows the result for the DTP-doped OPC-5. There is no evidence of intrinsic trapping, similar to the undoped OPC-1. This is consistent with the fact that DTP is not a trap for either TTA or TAPC.

Trapping at Strongly Absorbed Wavelength

The result of Figure 6 shows essentially no trapping for the undoped OPC-6, which employs a fully pigmented CGL with 100% light absorption at 780 nm. In this case, photogeneration is at the CTL/CGL interface, thus recombination is fully minimized. And with no traps present in the system, no intrinsic trapping is expected. The same result is seen and expected for the DTP-doped OPC-10.

The results of Figures 7 and 8 for the DAPM-doped OPC-7 and TAA-doped OPC-8 are different. As expected, there is no free-volume trapping for neither case; however, intrinsic CTL trapping is clearly apparent, especially for the more efficient trap TAA.

We can define free-volume trapping as the difference between the toe voltage 24 hours after incubation and the toe voltage at complete free-volume equilibrium (above 25 days for the present systems). The difference between the oxidation potential of the majority transport material TTA and that of the dopant molecules is the "trap depth". Thus we can produce the plots of Figure 9, showing the effect of trap depth on free-volume trapping. Three observations are made:

(1) There is no free-volume trapping for the 100% pigment-fully-absorbing CGL, no matter what the trap depth of the dopant molecule.

(2) The free-volume effect is more pronounced for the aggregate/5 wt% pigment CGL, at the weakly absorbed 780-nm compared to 690-nm where the aggregate is strongly absorbing.

(3) Above 0.20 V trap depth, free-volume trapping is almost completely supplanted by intrinsic trapping.

Intrinsic trapping is defined as the difference between the toe voltage at complete free-volume equilibrium for a system doped with a given guest molecule, and that of the undoped system at the same condition. Figure 10 shows the effect of trapping depth on intrinsic trapping. At about 0.15 V trap depth, intrinsic trapping increases steeply.

Summary & Conclusions

We have studied the free-volume trapping phenomenon in multi-active photoconductors doped with molecules of various oxidation potentials. These studies have made it possible to isolate free-volume from intrinsic trapping. We have reconfirmed the role of the charge generation layer and the importance of surface and bulk charge generation. Free-volume trapping is dominant at trap depth below 0.2 V. Above that, intrinsic trapping completely dominates at the trap concentration level of the experiment. Lower trap concentration will most likely delay the dominance of intrinsic trapping.

References

1. M. F. Molaire, "Free-Volume Trapping in Single-Layer Aggregate Photoconductors", IS&Ts Eighth International Congress on Advances in Non-Impact Printing Technologies, 220 (1992).

2. M. F. Molaire, US patent 5,232,804.

3. M. F. Molaire, "Free-Volume Trapping in Multi-active Photoconductors", IS&Ts 14th International Congress on Advances in Non-Impact Printing Technologies, 486, (1998).

Table 1. OPC Formulations

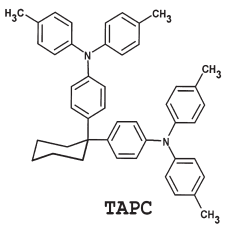
Lexan	18					
TTA	16.2					
Dye1	2.9					
Dye2	0.45					
IR Pigment	2.25					
Others	1.86	**CGL-1**	**CGL-2**	**CGL-3**	**CGL-4**	**CGL-5**
Dopant	**0.1 mole**	none	DAPM	TAA	DEH	DTP
Oxidation Potential			0.74 V	0.68 V	0.63 V	0.96 V

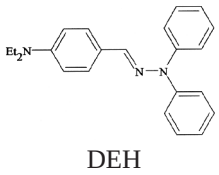
	CGL-6
Binder	50wt%
Pigment	50wt%

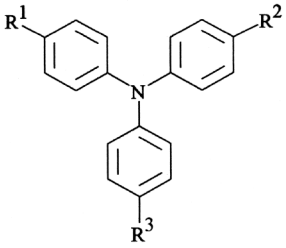
	Wt (g)					
Binder	42.1					
TTA	1.33					
TAPC	1.33	**CTL-1**	**CTL-2**	**CTL-3**	**CTL-4**	**CTL-5**
Dopant	**0.1 mole**	none	DAPM	TAA	DEH	DTP
Oxidation Potential			0.74 V	0.68 V	0.63 V	0.96 V

OPC-1	OPC-2	OPC-3	OPC-4	OPC-5
CTL1	CTL2	CTL3	CTL4	CTL5
CGL1	CGL2	CGL3	CGL4	CGL5

OPC-6	OPC-7	OPC-8	OPC-9	OPC-10
CTL1	CTL2	CTL3	CTL4	CTL5
CGL6	CGL6	CGL6	CGL6	CGL6



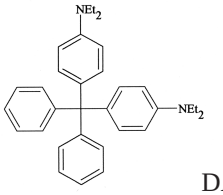




DTP, $R^1 = R^2 = CH_3$; $R^3 = H$

TAA, $R^1 = R^2 = R^3 = OCH_3$

TTA, $R^1 = R^2 = R^3 = CH_3$



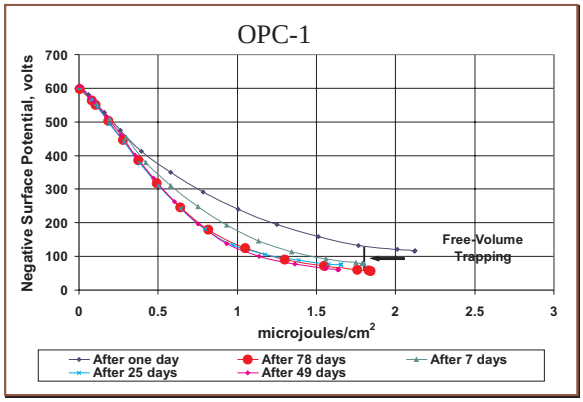


Figure 1 Trapping in undoped aggregate/5 wt% pigment CGL @ 780-nm exposure

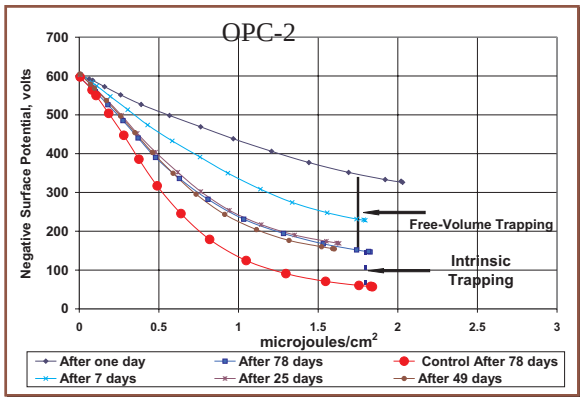


Figure 2 Trapping in DAPM-doped aggregate/5 wt% pigment CGL @ 780-nm exposure

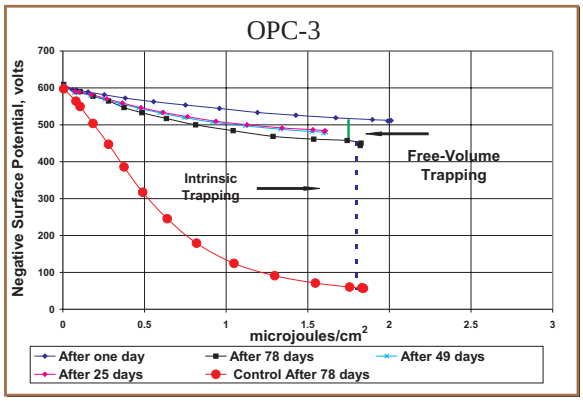


Figure 3 Trapping in TAA-doped aggregate/5 wt% pigment CGL @ 780-nm exposure

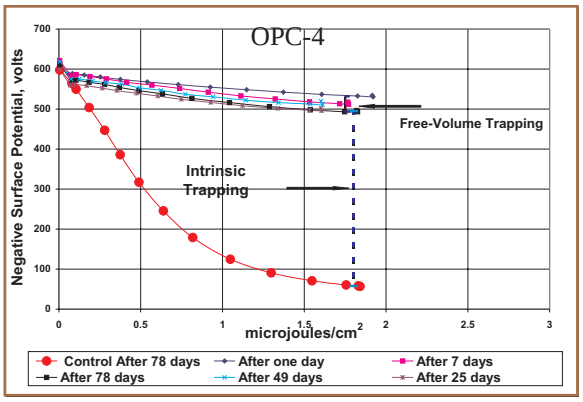


Figure 4 Trapping in DEH-doped aggregate/5 wt% pigment CGL @ 780-nm exposure

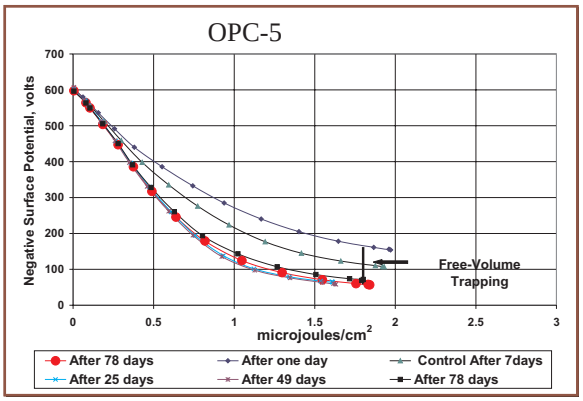


Figure 5 Trapping in DTP-doped aggregate/5 wt% pigment CGL @ 780-nm exposure

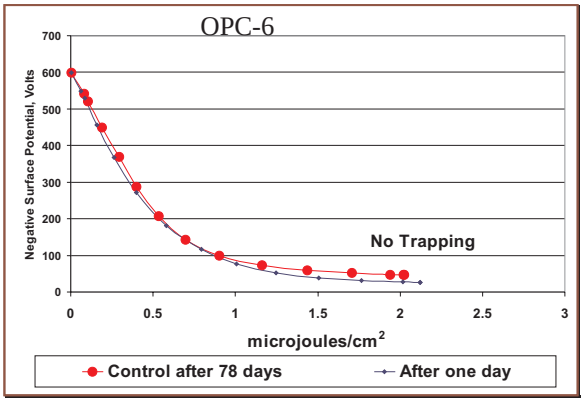


Figure 6 Trapping in undoped-100% pigment CGL @ 780-nm exposure

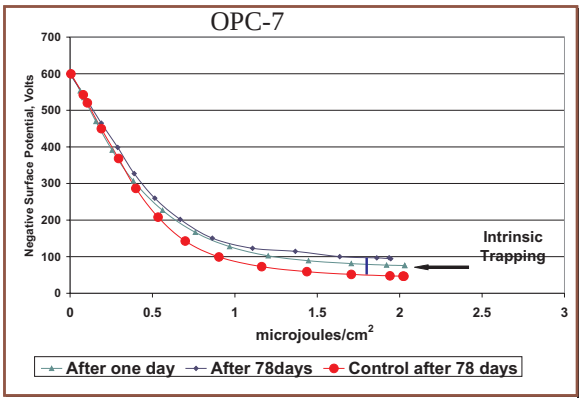


Figure 7. Trapping in DAPM-doped 100% pigment CGL @ 780-nm exposure

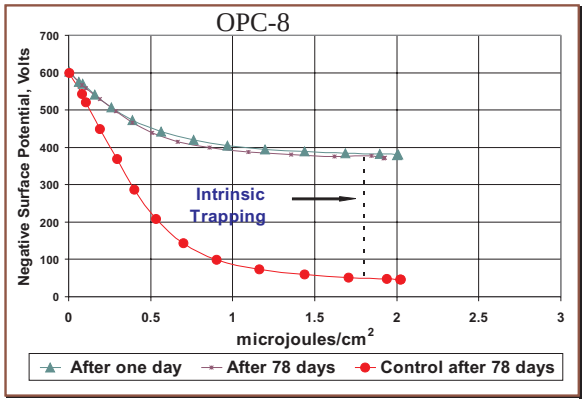


Figure 8. Trapping in TAA-doped 100% pigment CGL @ 780-nm exposure

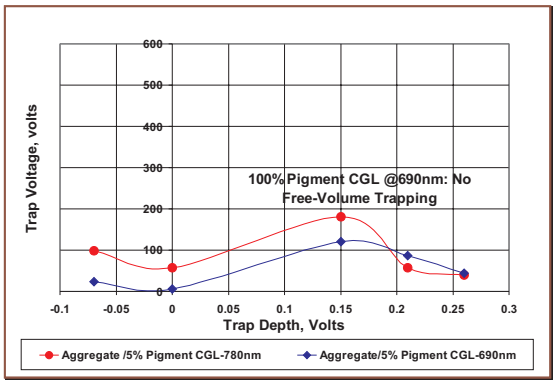


Figure 9 Free-volume trapping Vs trapping depth

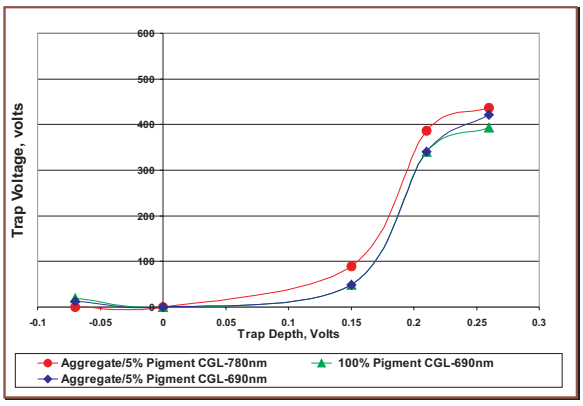


Figure 10. Intrinsic trapping Vs trapping depth