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# Analyzing hysteresis behavior of capacitance-voltage characteristics of IZO/C<sub>60</sub>/pentacene/Au diodes with a hole-transport electron-blocking polyterpenol layer by electric-field-induced optical second-harmonic generation measurement

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## Abstract

By using electric-field-induced optical second-harmonic generation (EFISHG) measurement, we analyzed hysteresis behavior of capacitance-voltage (C-V) characteristics of IZO/polyterpenol (PT)/C<sub>60</sub>/pentacene/Au diodes, where PT layer is actively working as a hole-transport electron-blocking layer. The EFISHG measurement verified the presence of interface accumulated charges in the diodes, and showed that a space charge electric field from accumulated excess electrons (holes) that remain at the PT/C<sub>60</sub> (C<sub>60</sub>/pentacene) interface is responsible for the hysteresis loop observed in the C-V characteristics.

*Keywords:* hole-transport electron-blocking layer, insulator, EFISHG

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## 1. Introduction

Recently, organic devices such as organic field-effect transistors (OFETs) [1], organic light-emitting diodes (OLEDs) [2], organic solar cells (OSCs) [3] are attracting much interest in electronics. However, owing to the complicated multilayer structure of these devices, carrier injection, transport, accumulation, and trapping phenomena require further understanding in relation to carrier behaviors at organic-organic interfaces. In particular, understanding charges trapped in organic devices is important, as it holds a key for stabilizing on/off states of memory devices and for improving long-term stability of OFETs, OLEDs, and OSCs. The hysteresis behavior of an organic device strongly depends on both the properties of organic molecules used for fabrication of individual layers as well as the processing methods employed. One of the ways to characterize the hysteresis is by taking capacitance-voltage (C-V) measurements, a technique which has been established to investigate interfacial charge trapping of metal-insulator-semiconductor (MIS) diodes [4], on the basis of semiconductor device physics. Another way to analyze hysteresis is to directly probe accumulated charges that are responsible for the hysteresis. The electric-field-induced second-harmonic generation (EFISHG) measurement, which we have been developing, directly probes carrier motions in organic devices [5, 6], and is available for analyzing hysteresis behavior of C-V characteristics.

In this Letter, we analyzed C-V characteristics of the MIS structure diodes with polyterpenol insulating film, in combination with the EFISHG measurement. Polyterpenol is one of the non-synthetic environmentally friendly

alternatives to the majority of organic precursors which pose an environmental hazard [7], an impediment for the development of environmentally sustainable technologies. The film of polyterpenol is obtained through plasma polymerization of terpinen-4-ol, a monoterpene alcohol component of the essential oils of several plants. The optically transparent polyterpenol thin film demonstrated good electrical insulating performance and is characterized by good stability against environmental variations [8]. In our previous work, we have reported the hole-transport electron-blocking property of the polyterpenol (PT) film using MIS diodes [9]. This property is quite interesting in that we can selectively introduce carriers into devices by the use of PT film. In this study, we demonstrated that PT layer incorporated into IZO/PT/C<sub>60</sub>/pentacene/Au diodes notably enhances the hysteresis behavior in the C-V characteristics of the diodes, and provided a mechanism to explain such a behavior. The C-V measurement implied that excess charges accumulated in the diode, causing threshold voltage to shift during the course of DC voltage cycles applied to the diode. By using the EFISHG measurement, we experimentally demonstrated that excess electrons and holes that remained at the PT/C<sub>60</sub> interface, were responsible for the hysteresis in the C-V curves.

## 2. Experimental

Figure 1 illustrates the structure of IZO/polyterpenol (PT)/C<sub>60</sub>/pentacene/Au diode used here. The polyterpenol layer is a hole-transport electron-blocking layer, as described in our previous paper [9]. A thin layer of polyterpenol was deposited onto the IZO electrode surface using RF plasma polymerization at

a pressure of 100 mTorr, RF frequency of 13.56 MHz, and RF power of 100 W. Terpinen-4-ol (Australian Botanical Products) vapors were released into the reactor at a constant rate. A layer of C<sub>60</sub>, pentacene, and Au electrode were successively deposited onto the polyterpenol thin film using vacuum evaporation technique, under a pressure of 10<sup>-5</sup> Torr at a deposition rate of around 1 nm/min. The resulting diodes were sealed in a glass vial with a desiccant. The capacitance of the polyterpenol, C<sub>60</sub>, and pentacene layers were  $C_1 = 1.7$  nF,  $C_2 = 5.6$  nF, and  $C_3 = 1.9$  nF, respectively. Here the electrode area was 3.1 mm<sup>2</sup>.

The current-voltage (I-V), capacitance-voltage (C-V) and EFISHG measurements were used for analyzing the hysteresis behavior of the C-V characteristics of the IZO/polyterpenol (PT)/C<sub>60</sub>/pentacene/Au diodes. In the I-V and C-V measurements, DC voltage was applied to the IZO electrode with reference to the Au electrode grounded, by applying a ramp voltage with a sweeping rate of around 0.3 V/s. The C-V characteristics were measured using an impedance analyzer at a frequency of 100 Hz and an AC amplitude of 0.1 V. C-V measurements were conducted in dark and under white light illumination (intensity, 1 mW/cm<sup>2</sup>).

Time-resolved EFISHG was employed to probe carrier motion in the IZO/polyterpenol (PT)/C<sub>60</sub>/pentacene/Au diodes, using the experimental setup portrayed in Fig. 1. As described in our previous papers [9, 10], upon application of an external DC voltage ( $V$ ) to the IZO electrode, charges  $+Q_m$  and  $-Q_m$  are induced on the IZO and Au electrodes, respectively, with a response time of  $\tau_{RC} = RC$ , where  $C$  is the total series capacitance of the diode and  $R$  is the external lead resistance. At time  $t \gg \tau_{RC}$ , holes and elec-

trons are allowed to enter the device and are subsequently transported along the electric field formed in the layer, if the PT and pentacene layers are not acting as carrier blocking layers. According to the Maxwell-Wagner (MW) effect, charges  $Q_1$  ( $Q_2$ ) accumulate at the polyterpenol/ $C_{60}$  ( $C_{60}$ /pentacene) interface, with a response time of  $\tau_1$  ( $\tau_2$ ). The accumulated charges are excess charges and they can be a source of space charge fields. As a result, in the presence of the accumulated charge  $Q_1$  and  $Q_2$ , the electric fields formed in organic layer is given as  $E_0 = E_m + E_{s1} + E_{s2}$ , where  $E_m$  is the Laplace field produced from charges on electrodes  $\pm Q_m$  and  $E_{s1}$  ( $E_{s2}$ ) is a space charge field from the accumulated charge  $Q_1$  ( $Q_2$ ).

Upon pulsed laser beam incidence to organic layers, the second-harmonic polarization  $P_{2\omega}$  (wavelength  $\lambda/2$ ) is produced in the layers due to electromagnetic coupling between the electric-field  $E_\omega$  of laser beam (wavelength  $\lambda$ ) and electrons in the molecules [11]. As a result, the EFISHG intensity  $I_{2\omega} \propto |P_{2\omega}|^2$  is described as [12]

$$I_{2\omega} \propto |\mathbf{P}_{2\omega}|^2 \propto |\epsilon_0 \chi^{(3)} : \mathbf{E}_0 \mathbf{E}_\omega \mathbf{E}_\omega|^2, \quad (1)$$

where  $\epsilon_0$  is the vacuum permittivity, and  $\chi^{(3)}$  is the third-order nonlinear susceptibility. The  $\chi^{(3)}$  is a function of laser beam wavelength, and is material dependent. That is,  $\chi^{(3)}$  notably increases at the SH wavelength, near the wavelength of optical absorption peak of material, due to resonant enhancement of electromagnetic coupling between the incident laser beam and electrons in the molecule. In the EFISHG measurement of the IZO/PT/ $C_{60}$ /pentacene/Au diodes, we measured EFISHG signals at the laser beam wavelength of 1000 nm (SH wavelength, 500 nm), and selectively measured electric fields in the  $C_{60}$  layer [13]. Note that the generation

of EFISHG from polyterpenol and pentacene layers is negligibly small at 1000 nm [9, 13]. Upon applying DC step voltage to the IZO electrode of the diode, in reference to the grounded Au electrode, charges  $Q_m$ ,  $Q_1$ , and  $Q_2$ , are successively accumulated on the electrodes and at the interfaces, respectively, and thus deform electric field in the  $C_{60}$  layer with time. Meanwhile, the EFISHG transients are generated in accordance with these three charging processes. The EFISHG transients were analyzed by using a filtering method, and charge densities and response times of charge accumulation processes were determined in the manner as described in our previous paper [10].

### 3. Results

Figure 2a shows the I-V characteristics of the IZO/polyterpenol (PT)/ $C_{60}$ /pentacene/Au diode in dark. The PT layer is working well as electrical insulator, and the current is  $< 20$  nA in the region  $-10 \text{ V} < V < +10 \text{ V}$ . Figure 2b shows the C-V characteristics of the diode in dark, where a hysteresis loop was observed in an anti-clock-wise direction. The capacitance was 0.8 nF at +10 V, which agreed well with the capacitance of the diode, calculated as 0.77 nF, by assuming that pentacene,  $C_{60}$ , and polyterpenol layers are acting as dielectric layers. On the other hand, the capacitance was 1.2 nF at -10 V, indicating that  $C_{60}$  and polyterpenol layers are acting as dielectric layers, while the pentacene layer is acting as a conductive layer. Figure 2 also shows I-V and C-V curves of the diode under illumination. The I-V curve never changed notably upon illumination, suggesting that the insulating property of the diode is not degraded by the illumination. Photocarriers might be

generated from the pentacene/C<sub>60</sub> double-layer [14], but the photocurrent was totally blocked by the insulating polyterphenol layer. On the other hand, under illumination, C-V curves showed a hysteresis loop in a clock-wise direction, in the opposite direction observed in the C-V curve in the dark. At the positive DC voltage  $V = +10$  V, capacitance was 2.4 nF, indicating that the PT layer is working as an insulator and the pentacene and C<sub>60</sub> layers are working as conductive layers. At the negative voltage  $V = -10$  V, capacitance was 2.1 nF, indicating that the PT and C<sub>60</sub> layers were electrically insulating while the pentacene layer was conductive. The capacitance of the diode observed under illumination were slightly greater than the capacitance of the polyterphenol layer, possibly due to the increase of the effective electrode area of the capacitor caused by the spreading of the charges on the electrode to the surroundings (edge effect). The turn-over of the hysteresis loop direction by illumination is discussed in section IV.

Figure 3 shows the EFISHG transients of the IZO/polyterphenol (PT)/C<sub>60</sub>/pentacene/Au diodes for positive step voltage application (Fig. 3a) and for negative step voltage application (Fig. 3b). Upon application of the positive step voltage, the EFISHG intensity smoothly increased with a response time of  $\tau_{RC}$  ( $= RC$ )  $\sim 10^{-7}$  s due to electrode charging on IZO and Au electrodes, where  $R$  ( $= 100 \Omega$ ) is the external lead wire resistance and  $C$  ( $\sim 1$  nF) is the capacitance of the diode. Subsequently, the EFISHG response for  $V = +5$  V saturated, indicating that carrier injection was negligible. On the other hand, the EFISHG intensity for  $V = +10$  V gradually increased with a response time of  $\tau_{1(hole)}$  ( $= 4.5 \times 10^{-6}$  s), and then decreased with a response time of  $\tau_{1(elec)}$  ( $= 1.2 \times 10^{-2}$  s). Results indicate that with a response time



of  $\tau_{1(hole)}$ , holes  $Q_{1(hole)}$  ( $= 5.2 \times 10^{-8}$  C/cm<sup>2</sup>) are injected from the IZO electrode and transported through the polyterphenol layer and accumulated at the C<sub>60</sub>/polyterphenol interface; then, with a response time  $\tau_{1(elec)}$ , electrons  $Q_{1(elec)}$  ( $= -7.7 \times 10^{-8}$  C/cm<sup>2</sup>) are injected from the Au electrode to the pentacene layer, and transported through the pentacene and C<sub>60</sub> layers, and accumulated at the C<sub>60</sub>/polyterphenol interface. The increase of the SHG intensity with a response time of  $\tau_{1(hole)}$  followed by the decrease with a response time of  $\tau_{1(elec)}$  accounts for this situation. As a result, in steady state at  $t \gg \tau_{1(elec)}$ , no charges remained in the diode,  $Q_{1(hole)} - Q_{1(elec)} \sim 0$ . Note that electrons inject from Au to pentacene and then accumulate at layer interface, in a manner as we reported previously [15, 16]. On the other hand, upon application of negative step voltage (see Fig. 3b), the EFISHG intensity increased with a response time of  $\tau_{RC}$  ( $\sim 10^{-7}$  s) attributed to the electrode charging. Subsequently, the EFISHG intensity increased with a response time of  $\tau_{2(hole)}$  ( $= 9.7 \times 10^{-5}$  s for  $V = -5$  V and  $4.0 \times 10^{-6}$  s for  $V = -10$  V), indicating that holes  $Q_{2(hole)}$  ( $1.6 \times 10^{-7}$  C/cm<sup>2</sup> for  $V = -5$  V and  $1.5 \times 10^{-7}$  C/cm<sup>2</sup> for  $V = -10$  V) injected from the Au electrode are accumulated at the pentacene/C<sub>60</sub> interface. Meanwhile electron accumulation is not allowed owing to the electron-blocking property of the polyterphenol layer. As a result, we cannot see the SHG decay with a response time of  $\tau_{1(elec)}$ .

#### 4. Discussion

Using the obtained EFISHG results shown in Fig. 3, we here discuss the hysteresis behavior of the C-V curves of the IZO/polyterphenol/C<sub>60</sub>/pentacene/Au

diodes. In dark, the hysteresis loop appeared in an anti-clock-wise direction. In more detail, with a decrease in the applied DC voltage from +10 V to -10 V, the capacitance gradually changed, but a clear and steeply increase was observed when the DC voltage reached at  $V = +4$  V, defined here as threshold voltage  $V_{th1}$ . The non-zero threshold voltage ( $V_{th1} \neq 0$ ) implied the presence of excess negative charges, i.e., electrons, which remain at the PT/C<sub>60</sub> interface during the C-V measurement. These remaining electrons form a space charge electric field pointing in the direction from the Au electrode to the C<sub>60</sub>/polyterpenol interface. That is, the space charge field from the excess electrons governs hole injection from the Au electrode to the pentacene layer. Although the above mechanism accounts well for the threshold voltage, it relies on the assumption of excess electrons being present at the PT/C<sub>60</sub> interface. In order to verify the proposed mechanism, direct evidence for the existence of excess electrons at the PT/C<sub>60</sub> interface is required. As shown in Fig. 3a, the EFISHG measurement identified that electrons  $Q_{1(elec)}$  were accumulated at the PT/C<sub>60</sub> interface. In more detail, the electrons  $Q_{1(elec)}$  at the interface formed a space charge field at the Au electrode  $E_{s1} = 1/d_3 \cdot C_2/(C_2 + C_3) \cdot Q_{1(elec)}/(C_1 + C_{23})$  while the external voltage forms electric field  $E_m = 1/d_3 \cdot C_{12}/(C_{12} + C_3) \cdot V$  ( $d_3$ : pentacene layer thickness,  $C_{12}$ : a series capacitance of the PT and C<sub>60</sub> layer,  $C_{23}$ : a series capacitance of C<sub>60</sub> and pentacene layers). At the threshold voltage  $V = V_{th1}$ , electric field  $E_{s1} + E_m$  should be zero,  $E_{s1} + E_m = 0$ , and in the region  $V < V_{th1}$  the electric field is pointing in the direction from the Au to the PT/C<sub>60</sub> interface. As a result, holes are allowed to be injected and the capacitance increases accordingly as obtained in the C-V curve. The thresh-

old voltage  $V_{th1}$  is calculated with the condition  $E_{s1} + E_m = 0$ , by using  $Q_{1(elec)}$  probed in the EFISHG measurement as  $V_{th1} (= -Q_{1(elec)}/C_1) = 1.8$  V. The calculated threshold voltage should agree with that observed in the C-V curve, but smaller than the experimental threshold voltage  $V_{th1} = 4$  V probably due to contribution from surface dipolar layer at organic-organic interface [17] and injection energy barrier at metal-organic interface [18, 19]. On the other hand, with increase of the applied voltage from -10 V to +10 V, the capacitance decreased and saturated at the threshold voltage  $V_{th2} = -4$  V. The decrease of the capacitance suggested that holes remained in the diode, and blocked hole injection from the Au electrode, resulting in a threshold voltage  $V_{th2} (< 0)$  in the C-V curve. However, this is again a speculation. The EFISHG measurement confirmed the excess holes  $Q_{2(hole)}$  accumulated at the  $C_{60}$ /pentacene interface under the negative DC voltage application, which form a space charge field at the Au electrode  $E_{s2} = 1/d_3 \cdot Q_{s2}/(C_{12} + C_3)$ . At the threshold voltage  $V = V_{th2}$ , the electric field  $E_{s2} + E_m = 0$ , and in the voltage region  $V > V_{th2}$  the electric field is pointing in the direction from the  $C_{60}$ /pentacene interface to the Au electrode, and prohibits hole injection from the Au electrode. As a result, the capacitance decreased in the region  $V > V_{th2}$  as shown in the C-V curve. Using the  $Q_{2(hole)}$  value from the EFISHG measurement, the threshold voltage is calculated as  $V_{th2} (= -Q_{2(hole)}/C_{12}) = -3.7$  V with the condition  $E_{s2} + E_m = 0$ . Result shows good agreement with the observed value of -4 V in the C-V curve. It is noteworthy that the hysteresis behavior in the positive voltage region ( $V_{th1} > 0$ ) was notably enhanced. That is, the hysteresis was clearly observed in the C-V curves of the diode with hole-transport electron-blocking PT layer. By

contrast, no hysteresis was observed in the C-V of the diode with electrically insulating polyimide layer (not shown here, see Ref. [20]). The EFISHG measurement of the IZO/PT/C<sub>60</sub>/pentacene/Au diode clearly showed that the excess holes  $Q_{1(hole)}$  accumulate at the PT/C<sub>60</sub> interface before electron accumulation  $Q_{1(elec)}$  is assisted (see the EFISHG transient at +10 V in Fig. 3a), whereas the EFISHG measurement of the IZO/polyimide/C<sub>60</sub>/pentacene/Au diode never showed such hole accumulation at the polyimide/C<sub>60</sub> interface as shown in our previous study [20]. These EFISHG results indicate that the hole-transport electron-blocking property of the polyterphenol is actively working to generate the hysteresis observed.

Finally, we discuss the hysteresis loop direction observed in the C-V curve. Under the illumination, the hysteresis loop in the C-V curve was in the clockwise direction, while in the dark it was in the anti-clock-wise direction. Upon illumination the IZO/PT/C<sub>60</sub>/pentacene/Au diode, C<sub>60</sub> and pentacene layers absorb the illumination and they become conductive, whereas the PT layer is as it is, i.e., an insulator. Accordingly, at the positive voltage  $V = +10$  V, capacitance value corresponded to that of the PT single layer capacitor. During the DC voltage cycle from +10 V to -10 V, excess electrons  $Q_{1(elec)}$  accumulate and remain at the PT/C<sub>60</sub> interface. Under the voltage  $V$  applied to the diode, the remained electrons  $Q_{1(elec)}$  occupy interfacial states and injected electrons  $Q'_{1(elec)}$  accumulate at the PT/C<sub>60</sub> interface, on satisfying the relation  $Q_{1(elec)} + Q'_{1(elec)} = C_1 V$ . At the threshold voltage  $V = V''_{th1}$ , injected electrons is zero,  $Q'_{1(elec)} = 0$ , giving threshold voltage  $V''_{th1} = Q_{1(elec)}/C_1$ . On the other hand, at the negative voltage  $V = -10$  V, capacitance value was that of PT/C<sub>60</sub> double-layer, indicating that holes are injected from Au to

the pentacene layer, and accumulated at the pentacene/ $C_{60}$  interface. Assuming that excess holes  $Q_{2(hole)}$  remain at the interface and form a space charge field  $E_{s2}$ , the electric field at the Au electrode  $E_{s2} + E_m$  should be zero at the threshold voltage  $V_{th2}''$  and it is in the direction from the  $C_{60}$ /pentacene interface to the Au electrode in the region  $V > V_{th2}$ , which results in the enhancement of electron injection from the Au electrode. The threshold voltage is calculated as  $V_{th2}'' = (Q_{2(hole)}/C_{12}) = +4$  V and capacitance increases in the voltage region  $V > V_{th2}''$  during the DC voltage cycle from -10 V to +10 V. Consequently, the C-V curve under illumination showed a hysteresis loop in a clock-wise direction, opposite to the hysteresis loop in the C-V curve in dark. Note that photocarrier injection from the IZO to the PT layer is possible due to the hole-transport electron-blocking property of the PT layer, but the no change of the I-V curve by illumination (see Fig. 2a) indicates that this possibility can be discarded. Also it is noteworthy that the pentacene/ $C_{60}$  double-layer system generates photovoltage  $V_{oc} = 0.36$  V [14], but its effect on the charge accumulation is minor, because the DC voltage applied in the measurements was fully greater than the photovoltage.

## 5. Conclusion

By using electric-field-induced optical second-harmonic generation (EFISHG) measurements, we analyzed the hysteresis behavior of capacitance-voltage (C-V) characteristics of the IZO/PT/ $C_{60}$ /pentacene/Au diodes where PT is actively working as a hole-transport electron-blocking layer. The EFISHG measurement showed that the excess electrons remained at the PT/ $C_{60}$  interface under the positive DC voltage +10 V, whereas excess holes accumulated

at the  $C_{60}$ /pentacene under the negative DC voltage -10 V. These excess electrons and holes remained in the diode and caused the hysteresis in the C-V characteristics.

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### Figure captions

**Figure 1:** IZO/polyterpenol (PT)/C<sub>60</sub>/pentacene/Au diode and optical setup for the time-resolved EFISHG measurement.

**Figure 2:** I-V (a) and C-V (b) characteristics of the IZO/polyterpenol/C<sub>60</sub>/pentacene/Au diode in dark and under illumination.

**Figure 3:** Time-resolved EFISHG signal transient after applying DC voltage  $V$ . (a)  $V > 0$ . (b)  $V < 0$ .

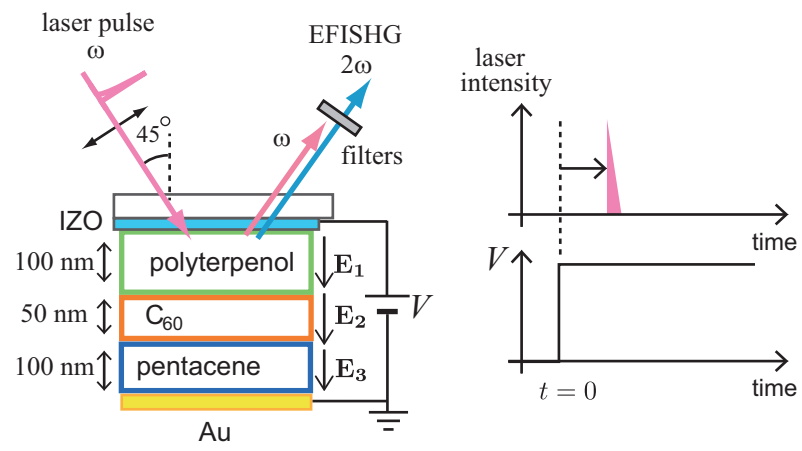


Figure 1: D.Taguchi et al.

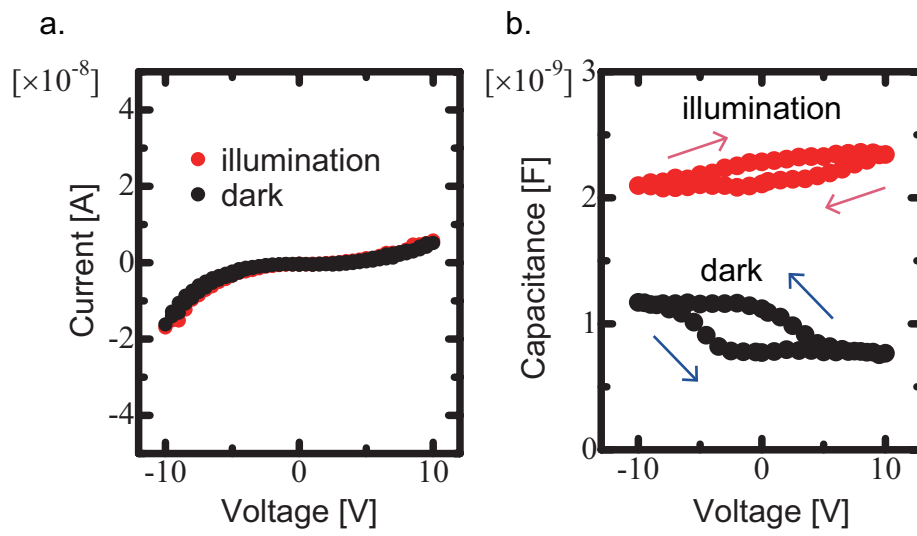


Figure 2: D.Taguchi et al.

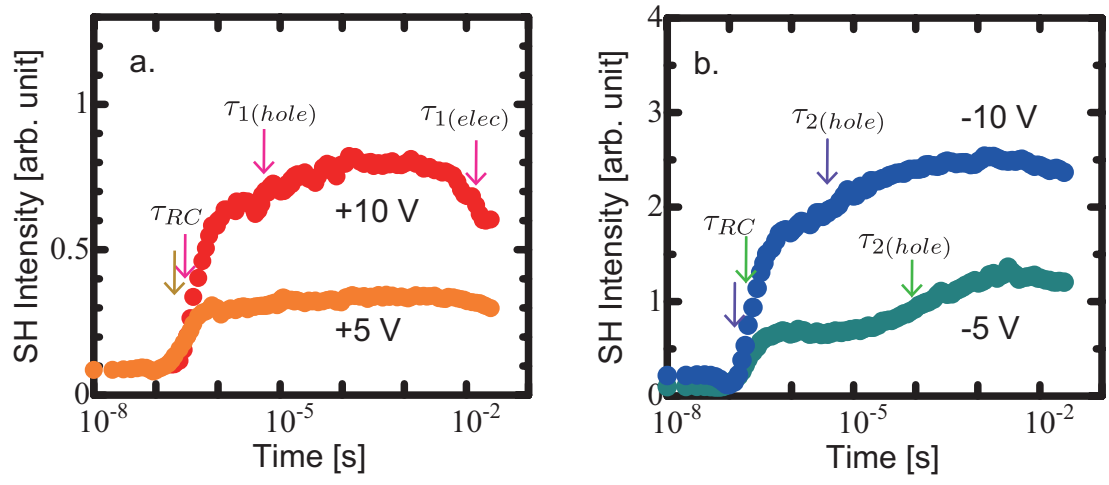


Figure 3: D.Taguchi et al.