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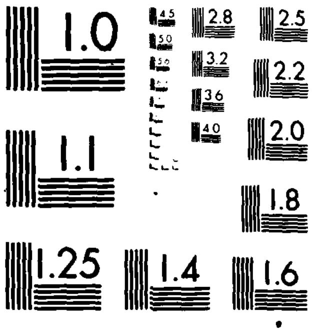

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SEMICONDUCTOR ELECTRODES. 43.

The Effect of Light Intensity and Iodine Doping ~~on~~ on the Stabilization of n-Silicon by Phthalocyanine Films

by

Patrick Leempoel, Mauricio Castro-Acuna, Fu-Ren F. Fan and Allen J. Bard

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(End of Abstract)

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Introduction

Although n-type silicon is an attractive semiconductor with respect to band gap energy and cost for photoelectrochemical (PEC) cells, it rapidly forms an insulating oxide film under irradiation in aqueous solution and passivates. Several techniques have been suggested to improve the stability of this semiconductor; these include derivatization of the electrode surface[1], coverage by thin metal layers[2], semiconductors[3], electroinactive polymers[4], or conductive polymers, sometimes undercoated with very thin metal layers[5-7]. To stabilize the n-Si electrode one must rapidly remove the photogenerated holes from the semiconductor surface and prevent water from reaching the Si where the photooxidation can occur. For this purpose phthalocyanine (Pc) films are potentially useful because of their hydrophobicity and semiconducting properties[8-10].

The recent report that n-Si can be stabilized by coating with Pc films[11] has prompted us to report our independent findings with several phthalocyanine systems under different light intensity conditions and with various redox electrolytes. We have found that while some stabilization can be achieved under very low irradiation intensities, no conditions could be found where long-term stability of n-Si occurred with Pc layers under light fluxes characteristic of solar radiation ($\sim$135 mW/cm^2).

Experimental

The electrodes were fabricated and treated as previously described[6] using n-Si (0.4 to 0.6 ohm-cm) obtained from Texas Instruments (Dallas, TX). Chemical etching was performed with HNO_3:HF:CH_3COOH (5:3:3 by volume) or with HNO_3:HF:CH_3COOH (3:1:1) with bromine (one drop per 70 ml) for 10 to 20 sec followed by a one min treatment with concentrated HF. The electrodes were thoroughly rinsed with deionized water and methanol prior to the deposition of the phthalocyanine films. These organic films were formed by vacuum sublimation (at 10^{-5} to 10^{-6} torr) as reported previously[10]; the thicknesses of the films ranged from 500 to 2000 Å (with coating times of 5 to 7 min). The coated silicon electrodes were kept under vacuum before use.

The light source was a 450 W xenon lamp (Oriel Corp., Stamford, CT) filtered through a 10 cm water filter combined with a 600 nm cut-off red filter (i.e., passing wavelengths >600 nm) or an 800 nm cut-off infra red filter to prevent light absorption and reflection by the iodine layer formed during the photoprocess[12] or by the phthalocyanine layer. The photocurrents generated by light absorption and photoeffects in the phthalocyanine layers are much smaller than those in the Si,[10,13] so that this contribution can generally be neglected. All chemicals were reagent grade and used without further purification. CuPc and H_2Pc were purchased from Kodak. Water was triply distilled from an alkaline potassium permanganate solution. All solutions were deaerated with nitrogen and the electrodes were immersed for 10 to 20 min. in the medium prior to the measurements.

A PAR Model 173 potentiostat and Model 175 programmer (Princeton Applied Research Corp., Princeton, NJ) and a Model 2000 X-Y recorder (Houston Instruments, Austin, TX) were used for the electrochemical experiments.

Results

Stability of Phthalocyanine-Covered n-Si Electrodes - Stable operation and photooxidation of $Fe(CN)_6^{4-}$ was recently reported for photoelectrochemical cells with n-Si/CuPc and n-Si/H_2Pc[11] at low light intensities. The effect of light intensity on the stability of a Pc-coated n-Si electrode is demonstrated by the experiments in Figures 1-3. When irradiated at low intensities (< 1 mW/cm^2) in I_3^-/I^-, Fe^{3+}/Fe^{2+}, or $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ solution, the n-Si/CuPc photoanode is obviously more stable than bare silicon. The very slow decay of photocurrent can be ascribed to the partial protection of the electrode surface by the organic layer. Similar behavior is found for all three redox solutions.

For a light intensity close to 100 mW/cm^2, where bare n-Si passivates completely in a few seconds, the photocorrosion process is remarkably decreased with the Pc coating, but the rate of formation of the insulating layer is very much dependent upon the nature of the redox couple. As compared with other redox couples, slower passivation occurred in iodide solutions where the decay of the photocurrent was only 35% in 10 min. The photocurrent-time behavior shown in Figures 1a and 2a represents some of the best results we have obtained with such systems in the absence of highly concentrated electrolyte. The rate of passivation of Pc coated n-Si in a given solution depended upon film thickness, stirring rate, and previous history of the electrode.

Iodine Doping of Phthalocyanine Films - A problem with the thicker Pc films used as coating is their high resistance which generally decreases the maximum photocurrents (i_{ph}) at a given light intensity compared to that initially observed on bare n-Si. For example, photooxidation of a 0.7 M solution of $Fe(CN)_6^{4-}$ at bare n-Si yields 11.5 mA/cm^2 while a n-Si/CuPc (800 Å) electrode under the same conditions produces only 0.6 to 1 mA/cm^2. However, much larger currents are found with Pc-coated electrodes in I_3^-/I^- solutions. Thus, the n-Si/CuPc (800 Å) electrode in 1 M I^-, 10^{-3} M I_3^- shows i_{ph} = 12 to 13 mA/cm^2.

Although the same trend is observed for electrodes with H_2Pc films, the limiting photocurrents are usually lower e.g. 2.5 mA/cm^2 in I_3^-/I^- vs. < 0.2 mA/cm^2 in 0.5 M Fe^{2+}/0.15 M Fe^{3+} at n-Si/H_2Pc (1000 Å) . These low photocurrents displayed by the n-Si/H_2Pc/Fe^{2+} system can be greatly enhanced by dipping the electrode for a few min. in an I_3^-/I^- medium. As shown in Figure 4, the photocurrent of an untreated electrode is low and decays rapidly while an I_3^- treated one shows significantly higher currents. The observed maximum might be caused by the oxidation of I_3^- (or I^- in the film, which in turn changes the conductivity of the film due to iodine doping[14]. The effect of iodine is also reflected in the faster response of a n-Si/CuPc electrode to light in a solution containing I_3^-/I^-, as compared to a solution containing I^- alone (Figure 5).

Evidence for iodine penetration into the Pc layer was also obtained by the spectroscopic analysis of a CuPc layer treated for 17 h in an I_3^-/I^- solution or with I_2 vapor. After treatment there was a general broadening of all absorption bands; the 617 nm peak was barely affected while the 695 nm band was slightly blue-shifted by 5 to 10 nm. These spectral features reverted to those of the untreated film upon exposure to air or vacuum expected for iodine penetration into the film. Iodine is known to be a dopant for Pc films[14-17] and improves their conductivity considerably.

The nature of the redox electrolyte influenced not only the magnitude of the photocurrent but also the shape of the i_{ph}-V curve (Figure 6). For a $Fe(CN)_6^{3-/4-}$ solution (Figure 6a), the increase of i_{ph} with V was relatively flat and the limiting i_{ph} was only reached at fairly positive potentials (0.8 V vs. SCE). The i_{ph}-V wave was significantly steeper in an I_3^-/I^- solution (Figures 6b and 6c). This behavior can also be attributed to doping by I_2 decreasing the film resistance. Similar behavior was observed for n-Si/H_2Pc electrodes.

The effect of iodine doping on the i_{ph}-V behavior is also illustrated in Figure 7. In a $Fe(CN)_6^{3-/4-}$ solution, under chopped illumination, the photocurrent at the n-Si/CuPc electrode rises rather slowly. Its limiting value is reached at large positive potentials (Figure 7a). When NaI is added to the medium, the curve becomes much steeper (Figure 7b). The magnitude of the limiting i_{ph} is only slightly affected, however, and is much smaller than that observed in the solution containing NaI alone (Figure 6c).

For all of the electrodes and solutions, i_{ph} was linearly related to the light intensity, at least up to 75 mW/cm^2 (Figure 8).

We also briefly investigated the effect of adding highly concentrated inert electrolyte (e.g. 11 M LiCl) to the solution. Under these conditions, the water activity is lowered significantly and this has been shown to improve the stability of semiconductor electrodes[6,18]. In such a solution (11 M LiCl, 0.5 M LiI, pH 0), a stable photocurrent of 1 mA/cm^2 at n-Si/H_2Pc was observed for more than 1.3 hr. However, slow photopassivation still occurred under these conditions as shown by a slight shift of the i_{ph}-V wave towards more positive potentials.

Discussion

Charge Transport in (n-Si/Pc) System - Photoelectrochemistry for the n-Si/Pc/solution system involves a number of different processes: charge transport in n-Si, charge transfer at n-Si/Pc interface, electron transfer reactions on any exposed silicon surface, charge transport through the Pc phase, charge transfer at the Pc/solution interface, and mass transport in the electrolyte solution. The movement of large ions, e.g. I^-, through the thin Pc film is probably very slow. However, penetration by iodine can occur. Thus, in the experiment in which $Fe(CN)_6^{3-/4-}$ and I^- are present simultaneously in the solution, the maximum photocurrent is only slightly changed because of the addition of iodide, this ion being oxidized slower at the CuPc interface (vide infra) and iodine being trapped by ferrocyanide. In the presence of I^- alone, however, the photocurrent is dramatically enhanced probably because of the induced doping by the photogenerated iodine. (Compare Figures 6c and 7.) Charge transport in n-Si and the mass transfer in the electrolyte solution at high concentration of redox species are not the processes limiting the photocurrent since the i_{ph} observed with the filmed electrode is near that of a bare n-Si electrode before it is passivated.

Facile electron transfer reactions on Pc-coated metal electrodes and photosensitized redox reactions on Pc-coated semiconductor electrodes have been recently demonstrated[8,19]. Photoexcitation of H_2Pc on WO_3 and TiO_2 results in a rapid oxidation of hydroquinone, ferrocyanide, and iodide, although the quantum efficiencies for these processes are extremely low[19]. Slower kinetics is observed for the photooxidation of I^- than for hydroquinone at SnO_2/CuPc[20]. All these examples demonstrate that holes generated either by photoexcitation or by charge injection from the substrate into the phthalocyanine film are able to oxidize suitable redox species.

The flat band potential, V_{fb}, of the n-Si electrodes used in this study at pH 0 is -0.2 V vs. SCE. (The onset potential of the photocurrent of bare n-Si electrodes at pH 0 is -0.15 V vs. SCE). The valence band edge of n-Si is thus more positive than the uppermost occupied energy levels of Pc used in this study[21,22]. The photogenerated holes in n-Si are thus energetically sufficient to oxidize (or inject into) Pc. Thus, the charge transport through the organic phase and the effect of the Pc layer on the generation and recombination mechanisms of photogenerated charge carriers in n-Si seem to be the two most important limiting processes in determining the photovoltammetric behavior of a (n-Si/Pc) system.

<u>Undoped Pc Films</u> - Without doping, Pc films usually show high resistivity[23,24]. When a potential is applied to a n-Si/Pc electrode, a large portion of the potential drop is absorbed across the Pc film. This reduces the band bending and the thickness of depletion layer of n-Si and thus decreases the photoeffect. In the low-biasing potential region, the

charge transport through the n-Si/Pc system would be limited by the resistance of the Pc thin film. As the electrode potential is made more positive, the light limiting process takes over. This photovoltammetric behavior is observed in the photooxidation of $Fe(CN)_6^{4-}$ as shown in Figure 6a. Note that the limiting photocurrent for the oxidation of ferrocyanide on n-Si/CuPc electrodes is at least one order of magnitude lower than that for the photooxidation of iodide on the same electrode at the same light intensity or that for the photooxidation of $Fe(CN)_6^{4-}$ on bare n-Si electrodes. This lower photoeffect is attributed to the enhanced recombination in the n-Si at the interface due to the impedance to the transport of holes away from the interface and through the thin Pc film. However, it is difficult to account for the linear dependance of this reduced limiting photocurrent on the light intensity (Figure 8b). Whether first order surface recombination[25] at n-Si/Pc interface becomes predominant here is not clear and requires further investigation.

The influence of the resistance of the Pc film on the rate of passivation of n-Si is also accommodated by this model. (Compare Figures 1 and 2.) With the high resistance film on the surface, the holes photogenerated in n-Si will accumulate at the n-Si/Pc interface and will oxidize the surface if water is present close to it. A scanning electron microscope study of the Pc thin films on n-Si electrodes does not reveal the presence of large cracks or defect structures. The films are homogenous and are made up of small grain with 50 to 100 Å diameters. This finding is consistent with that reported by Faulkner et. al.[9] Water penetration might occur through the grain boundaries.

Iodine Doped Pc Films - Evidence for significant improvement of the conductivities of various Pc materials by doping with iodine have been reported in a number of studies[14-17]. Iodine penetration into the films described in this report is supported by the spectroscopic analysis of the CuPc layer treated with an I_3^-/I^- solution or with I_2 vapor. Induced iodine doping of the Pc matrix results in a Pc film of higher conductivity as manifested by the steepness of the photovoltammetric waves and higher limiting photocurrents (Figure 6c). The photovoltammetric behavior cannot be attributed to the penetration of I^- through the Pc film, as suggested by the results shown in Figure 7. The highly conductive iodine-doped Pc films can remove photogenerated holes more rapidly from the silicon surface, as compared with an undoped film and thus better stabilizes the n-Si. Furthermore, only a small potential drop in the film occurs, and this increases the band bending in the n-Si and eliminates the recombination, as compared to highly resistive films. Higher photocurrents and fill factors and a linear dependence of the limiting photocurrent on light intensity similar to that found with the bare electrode before passivation are expected in such a system. The greater improvement in stability when a concentrated electrolyte is used can be attributed to a decrease in water activity[18] and a concomitant decrease in the rate of water penetration through the film.

Conclusion

At low light intensities, n-Si coated wih H_2Pc or CuPc behaves as a fairly stable photoanode, as previously reported. Excitation at higher light intensities (typical solar levels) leads to a rapid passivation by the reaction of the photogenerated holes and the small amounts of water that penetrate the film, even in the presence of a substance such as iodine which decreases the resistance of the film.

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Figure Captions

Figure 1 Photocurrent-time behavior for n-Si/CuPc (800 Å) in 1 M NaI, 10^{-3} M I_2 under stirred conditions. a) light intensity 72.5 mW/cm^2, bias potential 0.2 V vs. SCE; b) light intensity 0.3 mW/cm^2, bias potential 0.1 V vs. SCE.

Figure 2 Photocurrent-time behavior for n-Si/CuPc (800 Å) in 0.7 M $K_4Fe(CN)_6$, 0.05 M $K_3Fe(CN)_6$ under stirred conditions at 0.4 V vs. SCE. a) light intensity 114 mW/cm^2; b) light intensity 0.72 mW/cm^2.

Figure 3 Photocurrent-time behavior for n-Si/CuPc (500 Å) in 0.05 M $FeCl_2$, 0.05 M $FeCl_3$ under stirred conditions at 0.45 V vs. SCE for a light intensity of 0.44 mW/cm^2.

Figure 4 Photocurrent-time behavior for n-Si/H_2Pc (1000 Å) in 0.5 M $FeCl_2$, 0.5 M $FeCl_3$, 11 M LiCl at pH 0, bias potential 0.4 V vs. SCE. a) untreated electrode; b) iodine treated electrode.

Figure 5 Photocurrent-time behavior for n-Si/CuPc (1500 Å) in 0.2 M NaI, 0.5 M Na_2SO_4 at 0.2 V vs. SCE. a) new electrode; b) passivated electrodes in 0.2 M NaI, 4 X 10^{-3} I_2, 0.5 M Na_2SO_4 at 0.2 V vs. SCE; c) new electrode; d) passivated electrode.

Figure 6 Photovoltammetric curves for n-Si/CuPc under stirred conditions, scan rate 50 mV/s. a) n-Si/CuPc (800 Å) in 0.7 M $K_4Fe(CN)_6$, 0.05 M $K_3Fe(CN)_6$ at 72.5 mW/cm^2; b) n-Si/CuPc (800 Å) in 1 M NaI, 10^{-3} M I_2 at 0.73 mW/cm^2; c) n-Si/CuPc (800 Å) in 1 M NaI, 10^{-3} M I_2 at 72.5 mW/cm^2.

Figure 7 Photovoltammetric curves for n-Si/CuPc (800 Å), chopped light intensity 70 mW/cm^2, scan rate 50 mV/s. a) in 0.7 M $K_4Fe(CN)_6$, 0.05 M $K_3Fe(CN)_6$; b) in 0.7 M $K_4Fe(CN)_6$, 0.05 M $K_3Fe(CN)_6$, 1 M NaI. Electrode is partially passivated due to previous measurements in ferrocyanide solution.

Figure 8 Light intensity dependence of limiting photocurrents. $I_o \sim 70$

mW/cm^2. a) n-Si/H_2Pc (1000 Å) in 0.5 M LiI, 10^{-3} M I_2, 11 M LiCl, pH 0; b) n-Si/CuPc (800 Å) in 0.7 M $K_4Fe(CN)_6$, 0.05 M $K_3Fe(CN)_6$; c) n-Si/CuPc (800 Å) in 1 M NaI, 10^{-3} I_2. Stirred conditions.

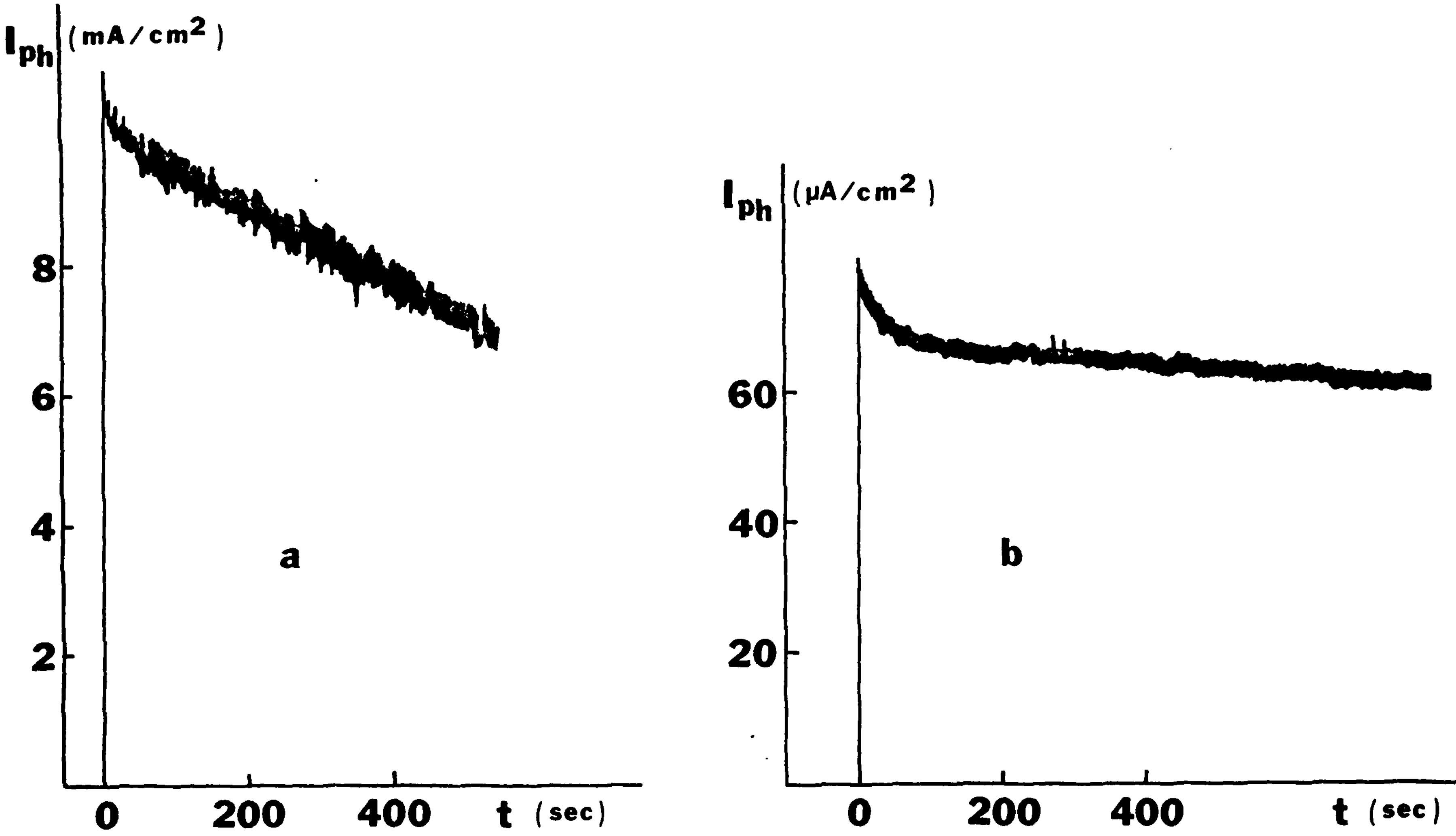
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Figure 1

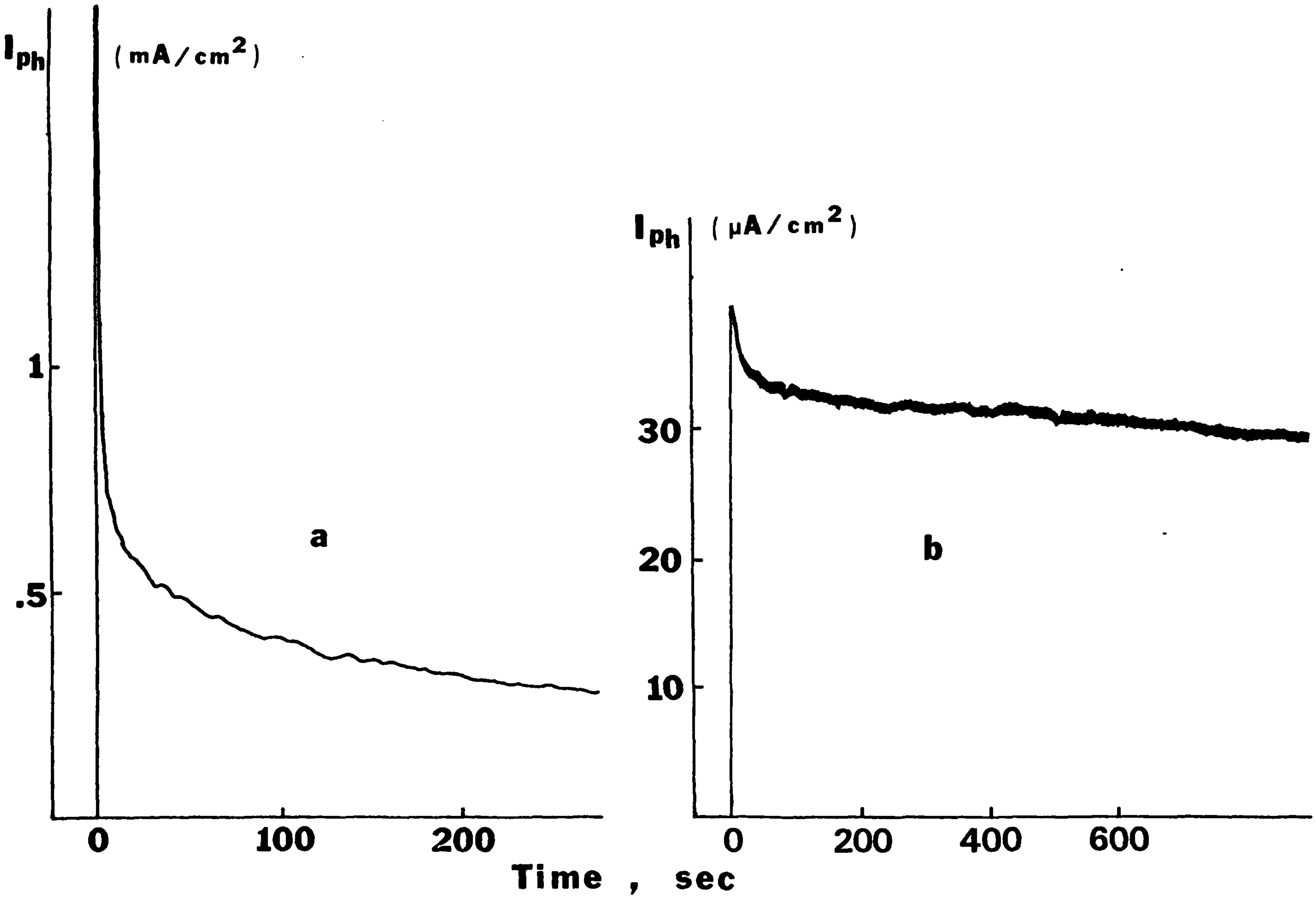
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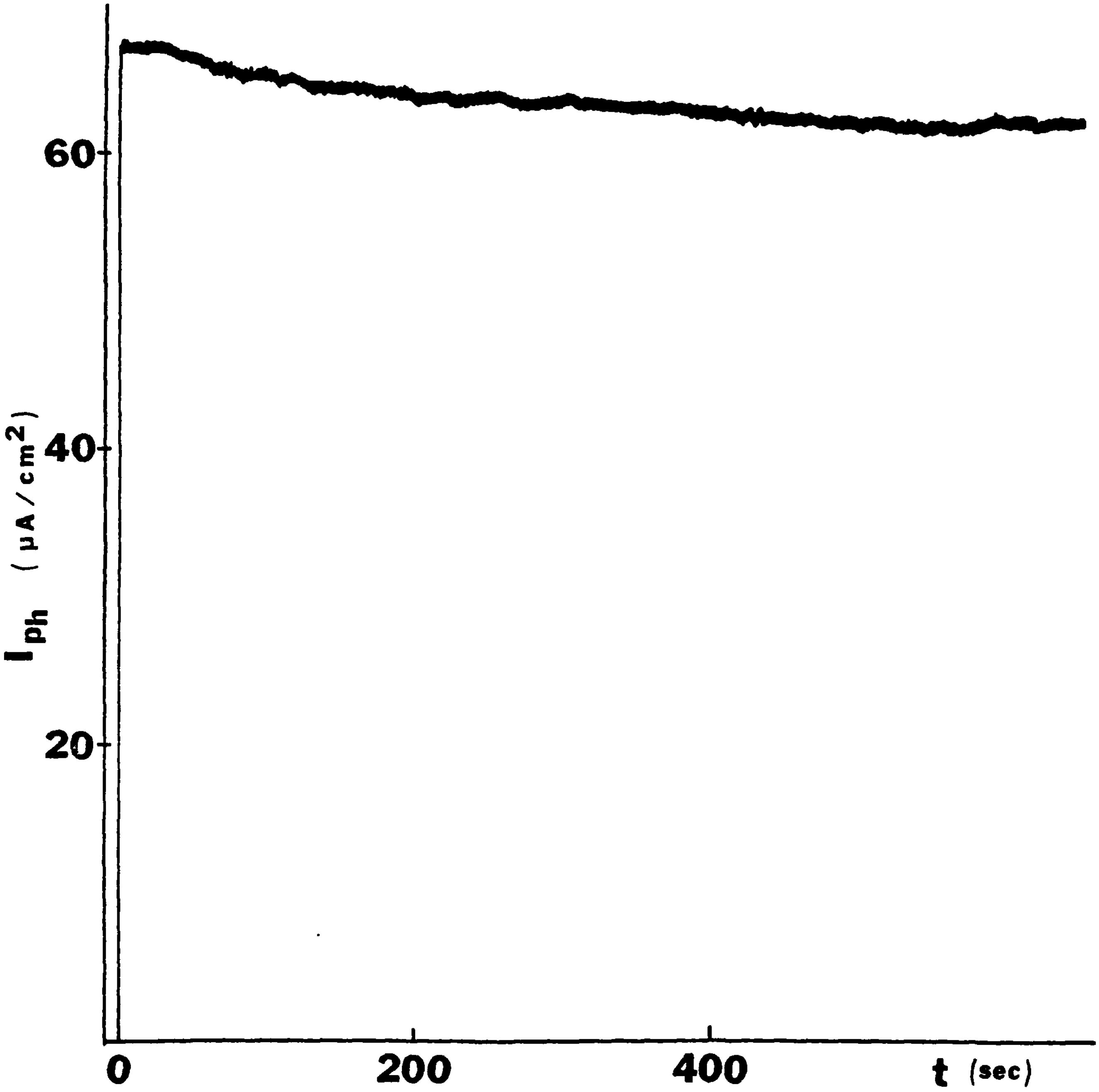
Figure 2



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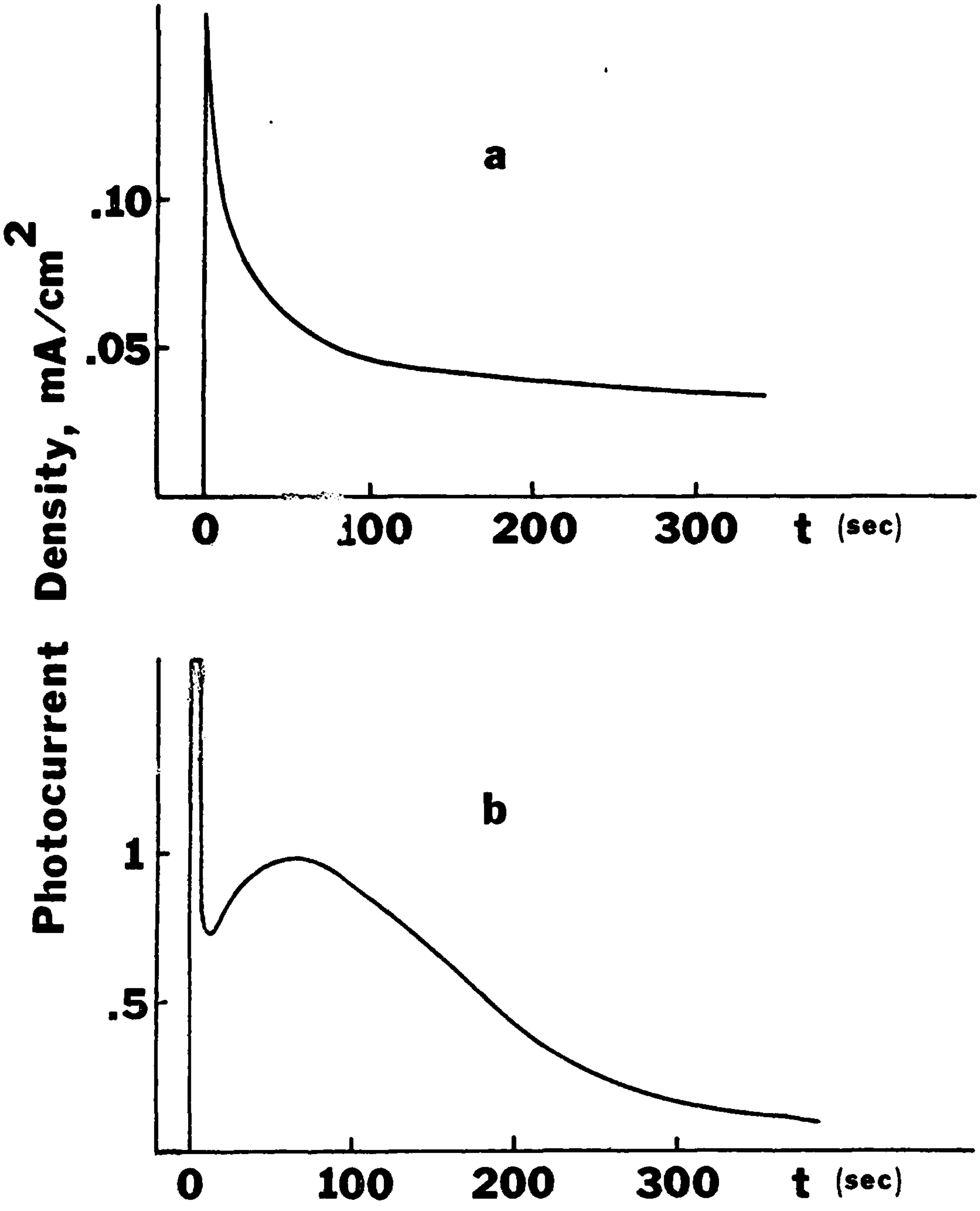

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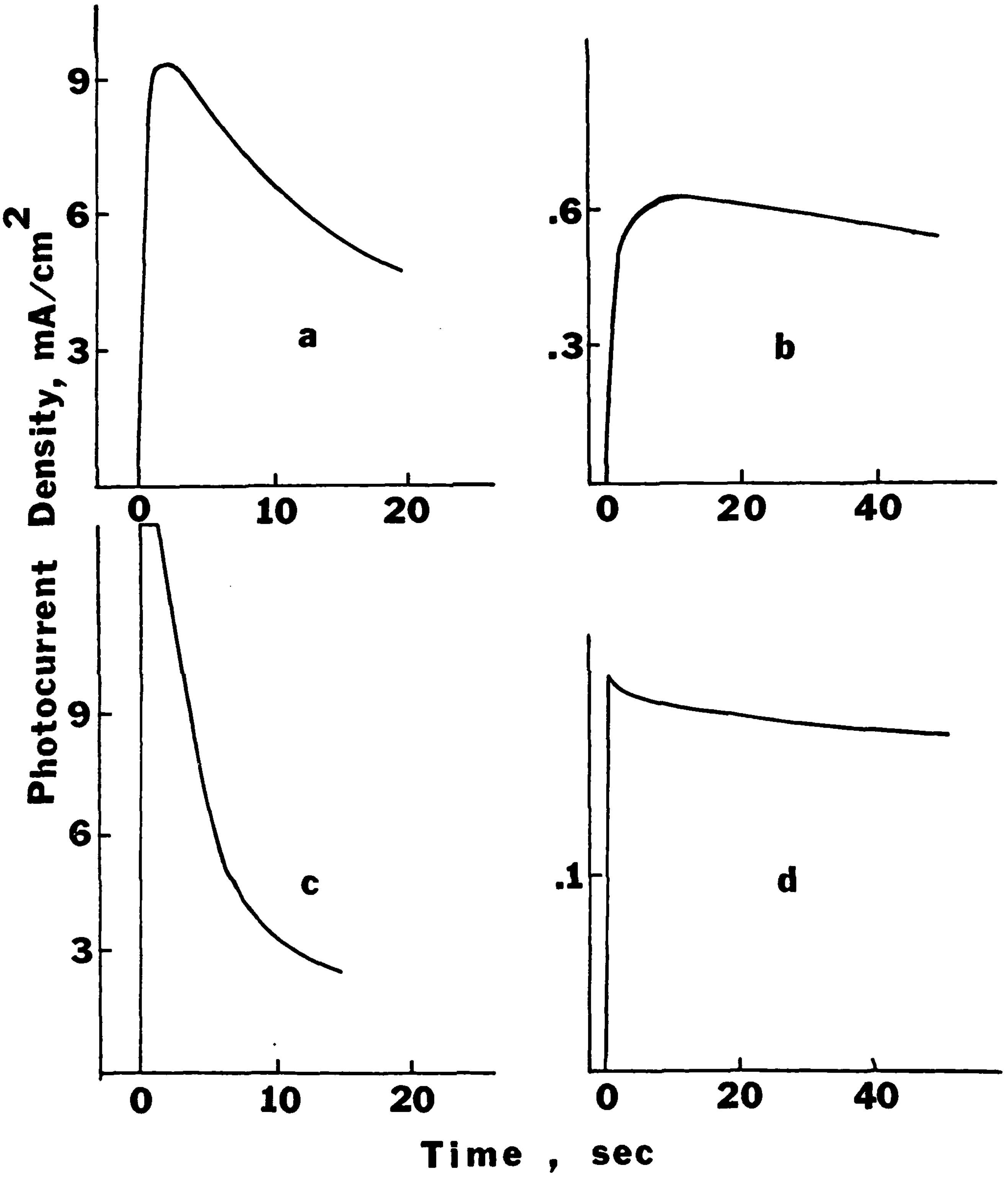
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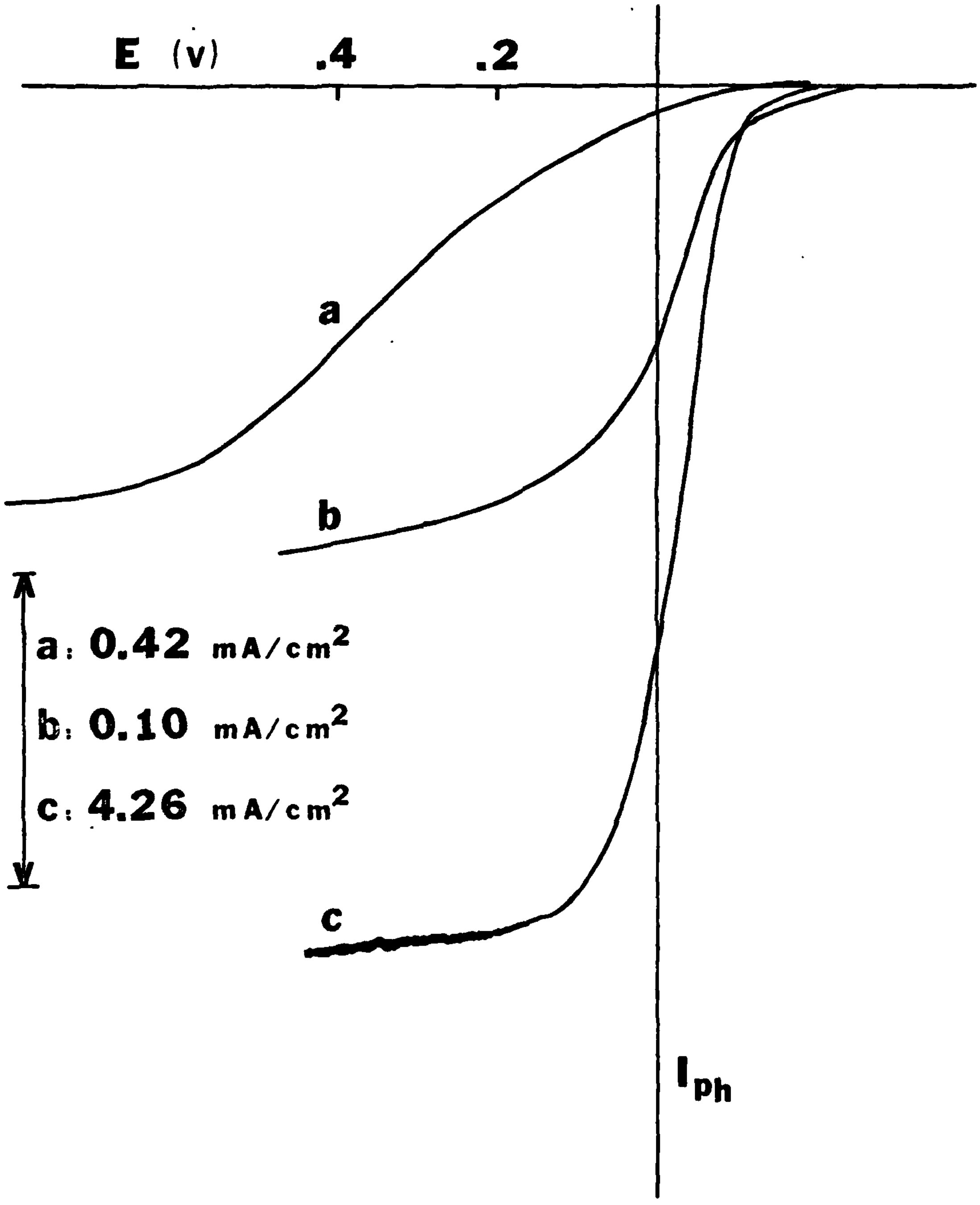
Figure 5



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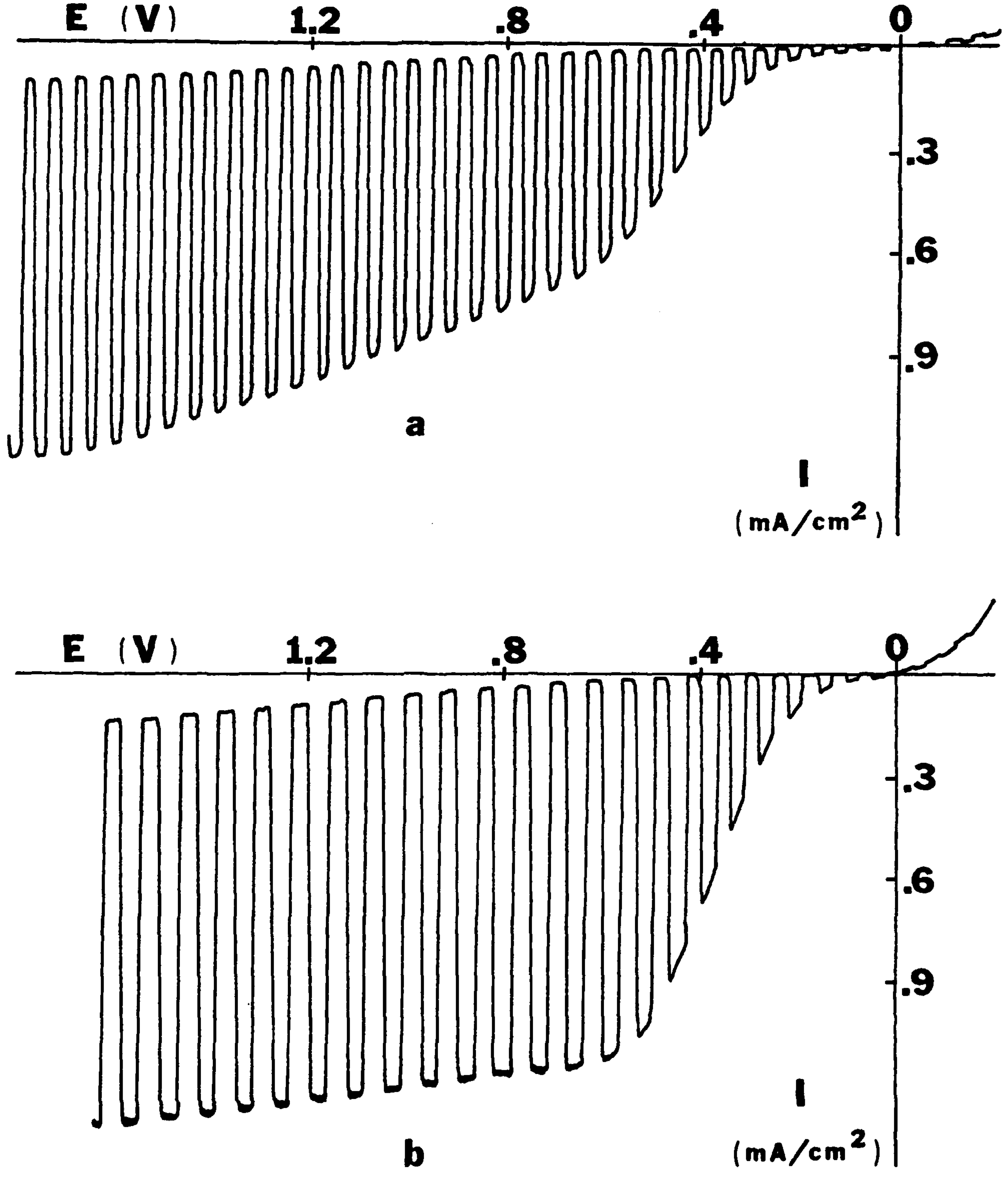
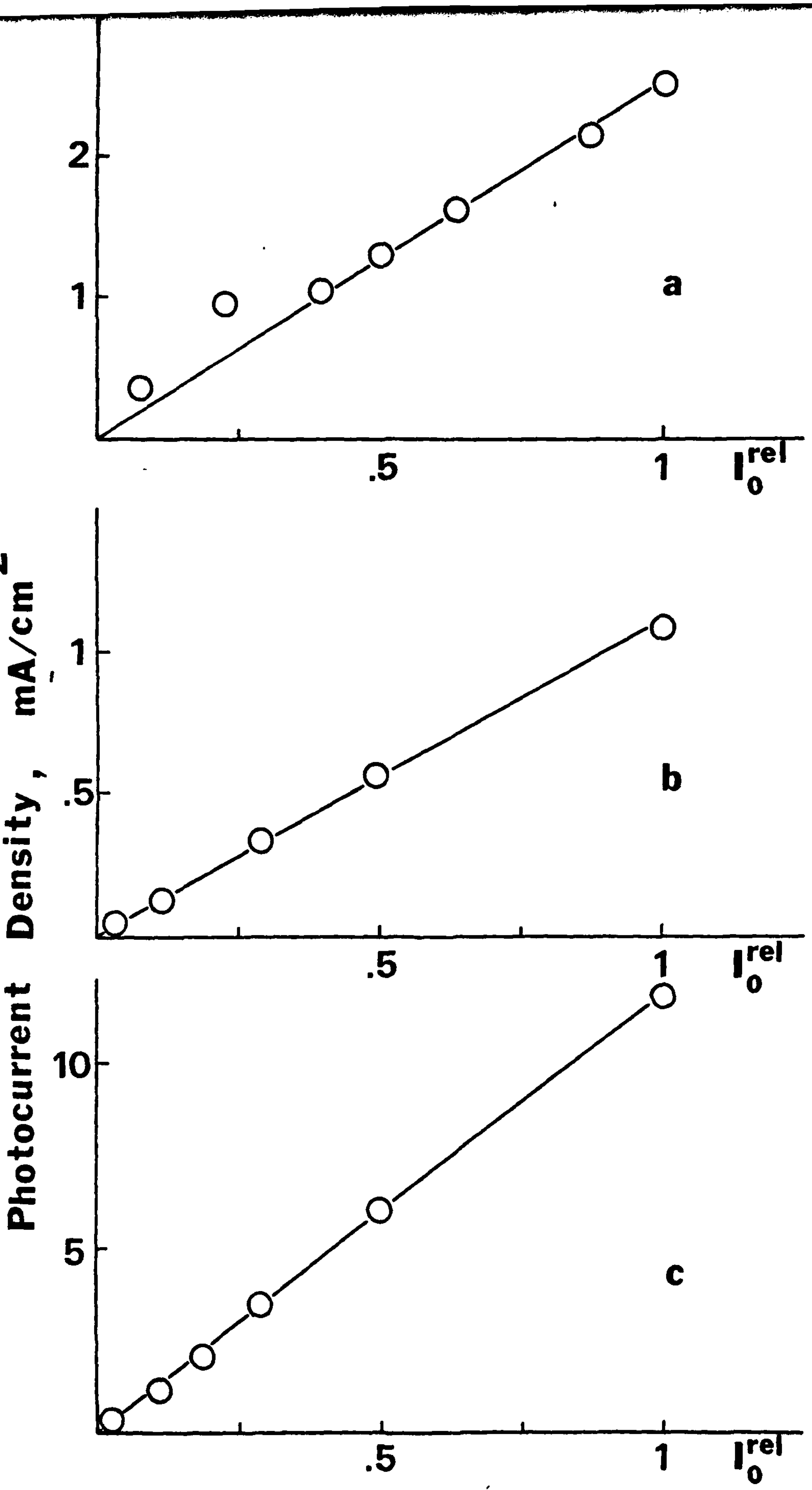


Figure 7



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a
.5
1
I_0^{rel}
Photocurrent Density, mA/cm^2
1
.5
b
.5
1
I_0^{rel}
10
5
c
.5
1
I_0^{rel}

Figure 8

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