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PHOTOFERROELECTRIC EFFECTS IN PLZT CERAMICS*

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ABSTRACT

A photoferroelectric effect described as photoassisted domain switching (PDS) is used to store high resolution, high contrast, nonvolatile optical information, including gray scale images in PLZT ceramics. Image storage is achieved by switching the ferroelectric remanent polarization while exposing the image on one of the indium tin oxide electroded surfaces of a PLZT plate, using near-UV light at the PLZT band gap energy (3.35 eV). PDS eliminates the photoconductive films required in previous PLZT image storage devices. Some characteristics of the PDS effect which apply to image storage and selective erasure are described. Image processing to achieve contrast enhancement is also discussed.

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BACKGROUND

Photoferroelectric (PFE) effects involving the photosensitivity of lead lanthanum zirconate titanate (PLZT) compositions to visible light have been studied and reported in the past. Micheron et al[1] were first to report PFE effects; i.e., photoinduced changes of refractive index (PCI), in PLZT X/65/35, with X = 2, 5, and 7.[2] They have since studied PCI extensively in PLZT 9/65/35.[3-6] Burgess et al[7] investigated PCI and photoconductivity in PLZT X/65/35, with X = 8, 9, and 10 and with various dopants added. Endo et al[8] observed photoenhanced changes in light scattering and dielectric constant in PLZT 7/65/35 when it was irradiated with 4880Å light while concurrently applying a saturating electric field. Micheron et al[9] studied nondestructive readout of image information in a PLZT 7/65/35-Se-Ge ferroelectric-photoconductor (FE-PC) memory by measuring current photoinduced by a scanning 4880Å laser beam.

We have found that PLZT photosensitivity is substantially enhanced by near-UV light at energies equal to or greater than the band gap (3.35 eV or 3700Å).[10,11] Furthermore, we have observed that illumination with near-UV light at relatively low intensities effectively decreases the electric field required to produce ferroelectric domain switching in PLZT ceramics. Therefore, we call this phenomenon photoassisted domain switching (PDS).[12]

PHOTOASSISTED DOMAIN SWITCHING

PDS is the process by which image storage and selective erasure is achieved in PLZT PFE image storage devices. There are at least three important physical effects which contribute to PDS.

1) Photoexcitation of carriers both from trapping centers in the PLZT band gap and across the band gap by near-UV light of energy equal to or greater than the band gap. Lower energy visible light can also photoexcite carriers

from trapping centers in the band gap, but the presence of visible light appears to lower the efficiency of the image storage process and to degrade the resolution of stored images.

2) Carriers photoexcited to the conduction state diffuse (with no field applied) or drift under the influence of an applied field to new trapping sites beyond the absorption depth of the PLZT. Retrapped carriers establish a space charge field E_{SC} which modulates the applied field E_A and aids in the domain switching process.[10,11]

3) A transient photocurrent i_{SC} is associated with photoexcited carriers which are retrapped to establish E_{SC}. Carriers remaining in the conduction state contribute to a steady state photovoltaic current i_{pv} which is driven by the bulk photovoltaic effect.[13-15] The photocurrents i_{SC} and i_{pv} both assist in domain nucleation and thereby aid the domain switching process.

Poled, ferroelectric-phase PLZT is also pyroelectric. Therefore, in addition to the effects enumerated above, photon absorption produces a temperature rise which results in a transient pyroelectric current i_{py}.[9,15]

The PFE image storage device consists simply of a thin flat plate of PLZT 7/65/35 with low resistance, transparent indium tin oxide (ITO) electrodes sputter deposited on the two major surfaces. If the ITO electrodes of a PFE device are short circuited and one of the surfaces of the PLZT is illuminated with near-UV light, all components of the photocurrent $i_{h\nu}$ are proportional to the light intensity I. This effect is illustrated in Fig. 1 which shows $i_{h\nu}$ plotted as a function of time for four different values of I. This sample and all others reported here were illuminated with a Hg-vapor lamp with a 700Å bandwidth filter centered at the 3650Å Hg line. The curves show the transient i_{py} and steady state i_{pv} for the light on condition and the transient i_{py} for the light off condition. From about 120 to 300 seconds the curves represent the steady state i_{pv}. The fine structure of the curves is probably due to Barkhausen-like domain switching associated with localized concentrations of space charge or photovoltaic fields.[16] The response of the recorder was too slow to record the transient i_{sc}. The results of Fig. 1 are summarized in Table I.

Under sample conditions similar to those described for Fig. 1, all the components of $i_{h\nu}$ are also proportional to the average remanent polarization P_r. This is illustrated in Fig. 2 which shows the transient i_{py} plus steady state i_{pv} for the light on condition and the transient i_{py} for the light off condition vs time for nine different values of P_r. From about 120 to 220 seconds the curves represent the steady state i_{pv}. Results of Fig. 2 are summarized in Table II.

Under open circuit conditions, the photocurrent charges the PLZT capacitance generating a macroscopic electric field E_i given by[15]

$$J = \kappa\alpha I + \sigma E_i \ , \qquad (1)$$

where J is the photocurrent density, κ is a constant depending on the nature of the absorbing center, the local environment, and the photon energy, α is the absorption coefficient, and σ is the electrical conductivity of the ceramic during illumination. In the steady state, the open circuit saturation field is

$$E_{i(S)} = -\kappa\alpha I/\sigma \ . \qquad (2)$$

Since $\alpha \propto I$, I/σ is a constant, and the open circuit steady state photovoltage during illumination is

$$V_{OC} = E_{i(S)}\, t = \text{constant}, \qquad (3)$$

where t is the PLZT plate thickness. This result is illustrated in Fig. 3.

The transient voltages from 0 to about 120 seconds are due to transient pyroelectric charge. From about 120 to 240 seconds, at which time the light is turned off, V_{OC} is a constant independent of I. When the light is turned off, E_i goes to zero and V_{py}, the voltage due to pyroelectric charge, reverses its polarity as the PLZT cools to ambient temperature. When I = 0, $\sigma \to 0$, so the time constant associated with open circuit pyroelectric voltage V_{py} is extremely long. Also, the change in open circuit voltage after I = 0 is proportional to the pyroelectric charge, and, hence, proportional to I in the illuminated state.

The short circuit and open circuit measurements described above illustrate the nature of the role of the space charge field E_{SC}, the photovoltaic field E_i, the photovoltaic current i_{pv}, and the photoconductance σ in PDS. The results also illustrate the pyroelectric properties of PLZT 7/65/35.

PFE IMAGE STORAGE

Photoconductive films required by previous PLZT FE-PC image storage devices[4,17-20] are not needed for PFE image storage. Image storage is achieved by exposing the image onto one of the ITO electroded surfaces of the PLZT plate using band gap light, and at the same time, switching the average remanent polarization through a portion of the hysteresis loop. The near-UV light, spatially modulated by the image, produces spatial modulation of the ferroelectric domain switching fields. This results in a corresponding spatial variation of the ferroelectric domains after the external switching voltage is removed. Localized variations of ferroelectric domain orientations produce related variations in light scattering[21,22] and surface deformation strains.[23] Hence, transmitted or reflected visible light is scattered or diffracted to reproduce the spatial modulation of the input near-UV light.

Either total or selective erasure of the stored image is achieved by uniformly illuminating the area to be erased with band gap light at about 10 mW/cm^2 minimum intensity and simultaneously switching the ceramic to its initial polarization state at saturation remanence. It has been observed that more energy is required for erasure than for storage of an image.[6] Also, if an image has been stored for several days, it is more difficult to erase than one stored for a few hours or less.

We have also demonstrated erasure by heating the ceramic to the ferroelectric-penferroelectric phase transition temperature T_t at which all domain structure disappears.[24,25] For PLZT 7/65/35, T_t is about 100 C. This erasure process has been achieved by passing a sheet current through one of the ITO electrodes to produce Joule heating.[25]

IMAGE CONTRAST ENHANCEMENT

After storage of a gray scale image in a PFE device, the sense of the image can be inverted from positive to negative, or vice versa, by switching the average remanent polarization away from that used to store the input image. The contrast can also be modified arbitrarily by simply switching the average remanent polarization to intermediate values between those which produce a positive or negative image. This effect is illustrated by the step density scale photographs of Fig. 4. Figure 4A is a photograph of the step density transparency used to store the image of Fig. 4B. The calibrated density variation is 0.5 optical density per step. Figure 4B is a photograph of an image of Fig. 4A stored in a 250 μm thick plate of 5 μm grain size PLZT 7/65/35. The average remanent polarization P_r of the ceramic in Fig. 4B was arbitrarily set at zero for reference purposes. When P_r was switched to $- 6.53\ \mu C/cm^2$, the maximum density step moved from position 1 in Fig. 4B to position 2 in Fig. 4C.

As P_r was switched to increasingly negative values as shown in Figs. 4D, 4E, and 4F, the maximum density step moved from position 2 to positions 3, 4, and 5. This technique of baseline subtraction in the stored image may be used to obtain contrast enhancement in incoherent images stored in a PFE device.

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FIGURE CAPTIONS

1. Short circuit photocurrent vs time for four different levels of light intensity I. (See Table I). PFE device consisted of a 5 μm grain size PLZT 7/65/35 plate, 7.84 cm^2 in area and 150 μm thick with sputter deposited ITO electrodes on both major surfaces. ITO sheet resistance ~ 3 ohms/square.

2. Short circuit photocurrent vs time for nine different values of remanent polarization P_r (See Table II). PFE device same as for Fig. 1.

3. Open circuit photovoltage vs time for four different levels of I. PFE device same as for Fig. 1.

4. Image contrast variation as a function of average remanent polarization for a PFE image storage device. (A) Input image step density scale; (B) Stored negative of (A) using an irradiance of 80 mW/cm^2; (C) Image in (B) after switching to $P_{r(av)} = -6.53\ \mu C/cm^2$; (D) Image in (B) after switching to $P_{r(av)} = -12.30\ \mu C/cm^2$; (E) Image in (B) after switching to $P_{r(av)} = -17.35\ \mu C/cm^2$; (F) Image in (B) after switching to $P_{r(av)} = -21.56\ \mu C/cm^2$.

TABLE I

Short Circuit Peak and Steady State Photocurrents

vs. Light Intensity (from Fig. 1)

Light On			Light Off	
Light Intensity I (mW/cm^2)	Peak ($i_{py} + i_{pv}$) ($A \times 10^7$)	Steady state i_{pv} ($A \times 10^8$)	Peak i_{py} ($A \times 10^7$)	Time Constant τ*
74.0	-2.95	-7.0	3.20	27
38.0	-1.70	-4.0	1.85	28
28.5	-1.30	-2.7	1.20	30
10.5	-0.50	-1.0	0.45	28

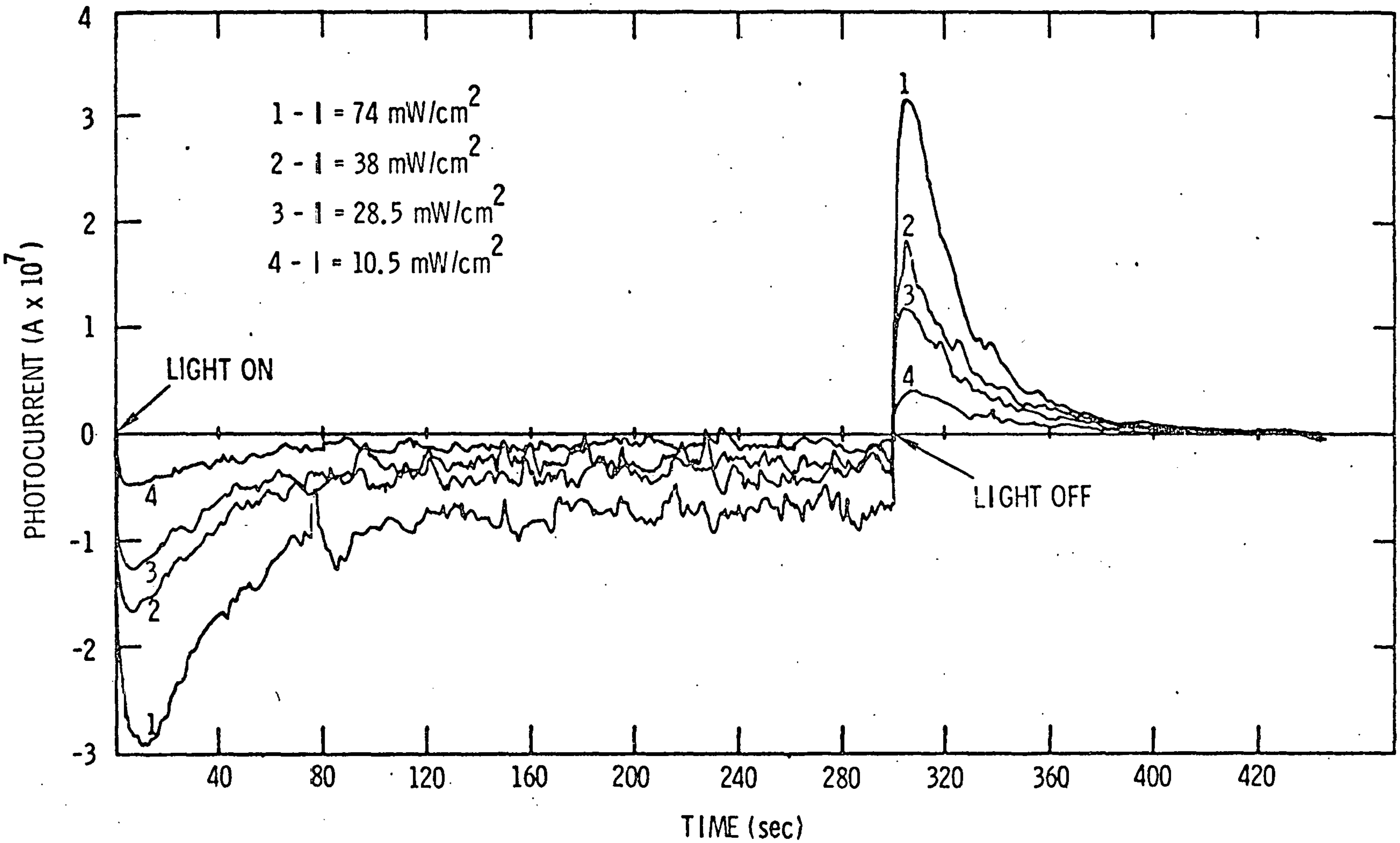
*Time constant associated with i_{py} after illumination is turned off.

TABLE II

Short Circuit Peak and Steady State Photocurrents vs. Average Remanent Polarization (from Fig. 2)

		Light On		Light Off	
Curve (Fig. 2)	P_r ($\mu C/cm^2$)	Peak ($i_{py} + i_{pv}$) ($A \times 10^7$)	Steady state i_{pv} ($A \times 10^8$)	Peak i_{py} ($A \times 10^7$)	Time Constant τ* (sec.)
0	31.10	-4.42	-9.5	3.38	28
1	25.00	-2.54	-5.5	2.70	27
2	15.80	-1.48	-3.6	1.70	28
3	3.80	-0.55	-0.5	0.55	18
4	0.77	-0.25	0	0.30	9
5	-2.30	-0.03	+0.6	0.03	2
6	-8.20	+1.41	2.5	-1.15	32
7	-13.00	2.25	4.2	-2.20	28
8	-18.00	2.87	6.5	-2.96	29

*Time constant τ associated with i_{py} after illumination is turned off.



1 - I = 74 mW/cm²
2 - I = 38 mW/cm²
3 - I = 28.5 mW/cm²
4 - I = 10.5 mW/cm²
LIGHT ON
LIGHT OFF
PHOTOCURRENT (A x 10⁷)
TIME (sec)
4
3
2
1
0
-1
-2
-3
40
80
120
160
200
240
280
320
360
400
420

FIG. 1

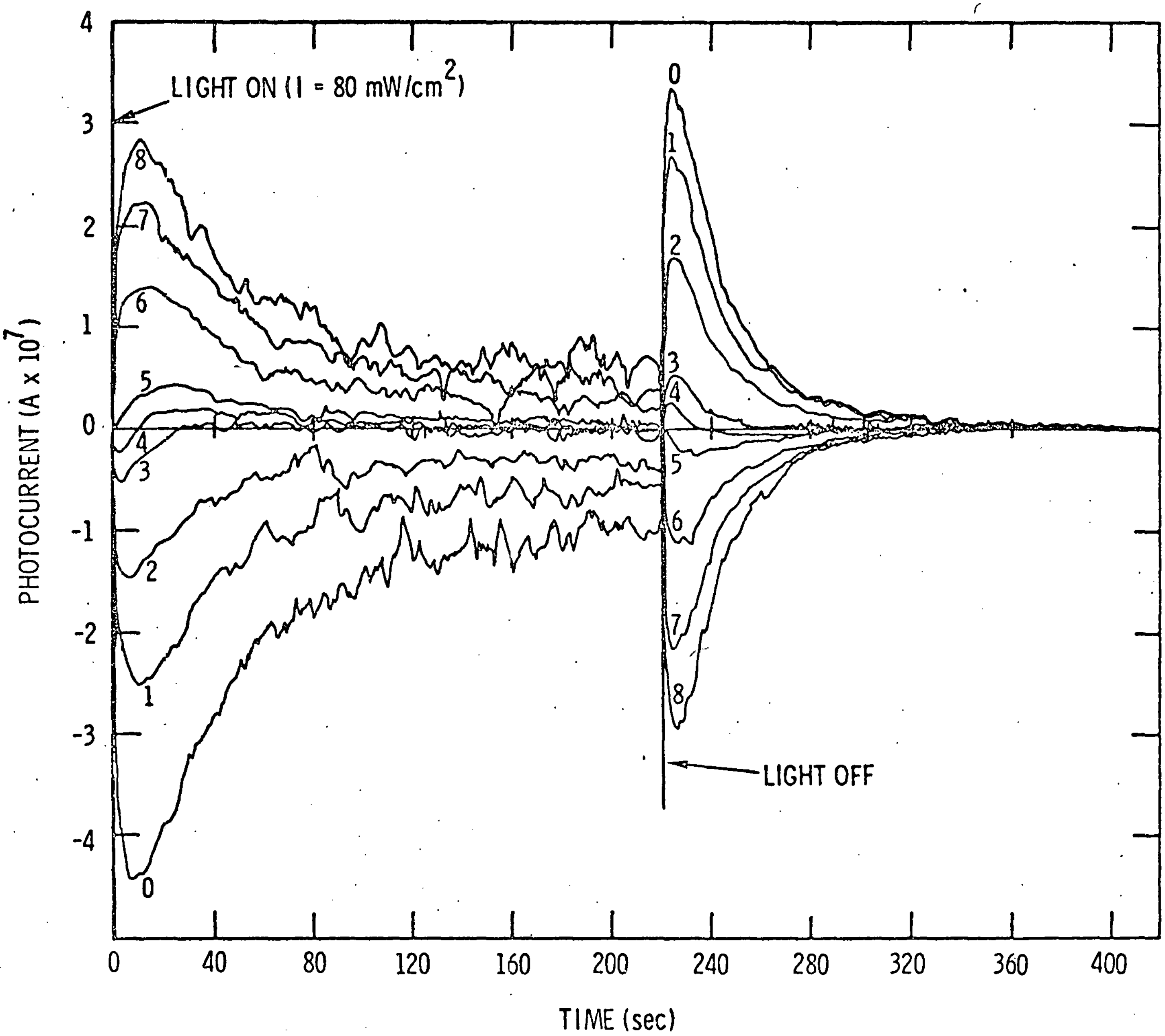

LIGHT ON (I = 80 mW/cm2)
LIGHT OFF
PHOTOCURRENT (A x 10^7)
TIME (sec)
4
3
2
1
0
-1
-2
-3
-4
0
40
80
120
160
200
240
280
320
360
400
8
7
6
5
4
3
2
1
0

FIG. 2

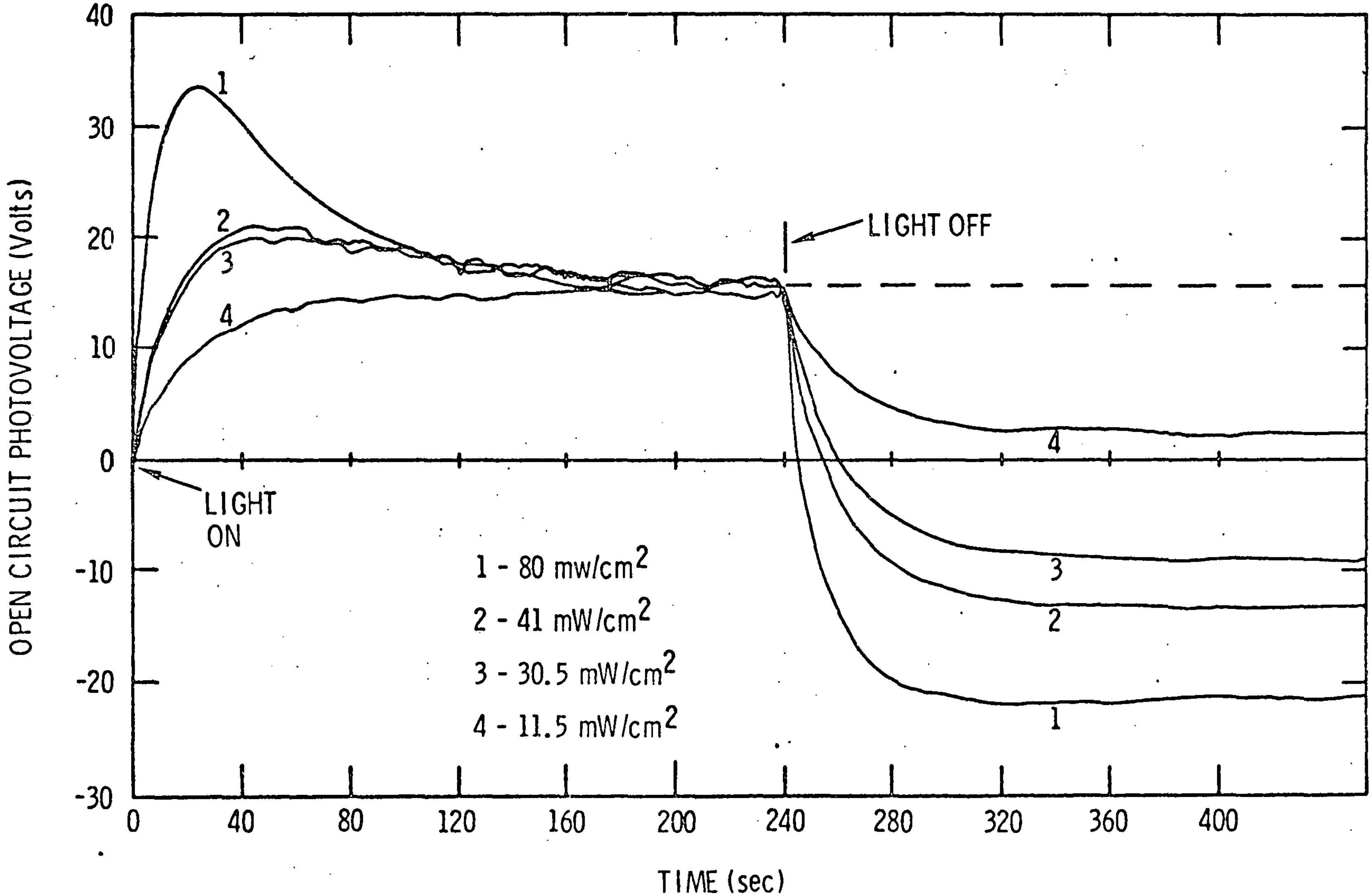
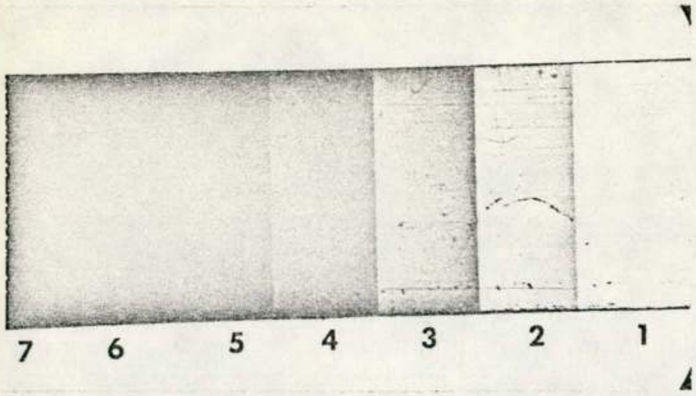
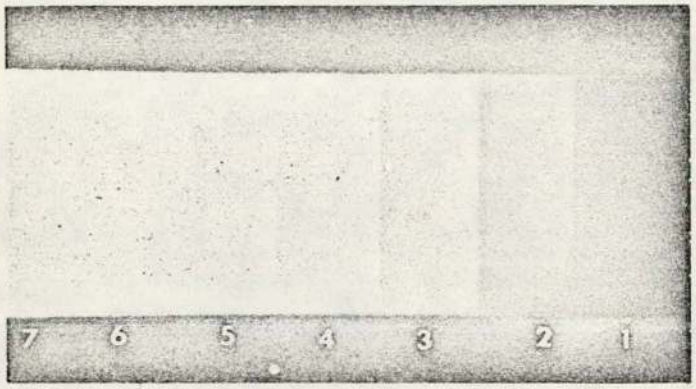

OPEN CIRCUIT PHOTOVOLTAGE (Volts)
40
30
20
10
0
-10
-20
-30
0
40
80
120
160
200
240
280
320
360
400
TIME (sec)
LIGHT ON
LIGHT OFF
1
2
3
4
1 - 80 mw/cm2
2 - 41 mW/cm2
3 - 30.5 mW/cm2
4 - 11.5 mW/cm2

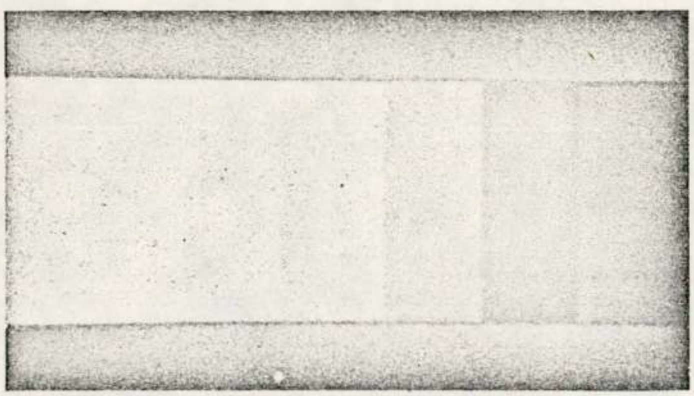
FIG. 3



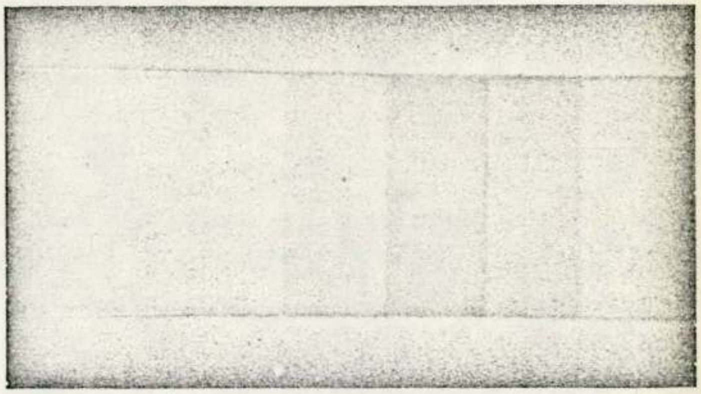
(A) Input Step Density Scale



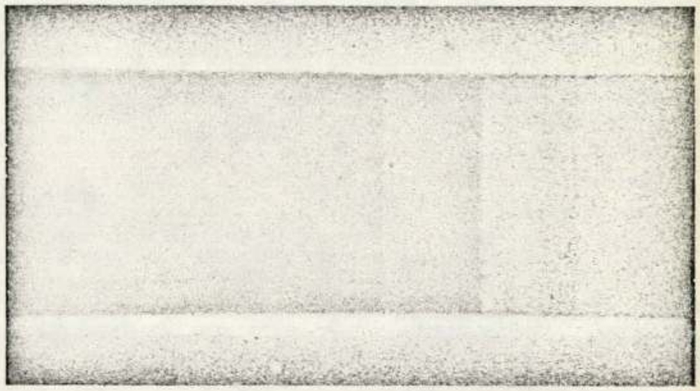
(B) Stored Negative of (A)
P_R(AV) = 0



(C) Image in (B) After Switching to P_R(AV) = -6.53 μC/cm^2



(D) Image in (B) After Switching to P_R(AV) = -12.30 μC/cm^2



(E) Image in (B) After Switching to P_R(AV) = -17.35 μC/cm^2

(F) Image in (B) After Switching to P_R(AV) = -21.56 μC/cm^2

FIG. 4