CHAPTER - 9

Effect of intensity of illumination on the PEC performances of both n-WSe_2 and p-WSe_2 photoelectrodes.

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9.1. INTRODUCTION :

The efficiency and behaviour of most photoelectrodes in PEC cell depend not only on the nature of the surface, nature of electrolyte, temperature of the electrolyte but also upon the intensity of the light with which the semiconductor-electrolyte interface is irradiated. The effect of electrolyte and its concentration has already been discussed in the earlier chapter. Since properties of PEC cells depend on the charactristic of incident light, the wavelength and intensity, author has described such studies on PEC cells based on tungsten diselenide in this chapter.

9.2. EXPERIMENTAL :

The grown n-type and p-type single crystals of WSe_2 as photoelectrodes and platinum grid as counter electrode are immersed in an aqueous iodine/iodide (by mixing 1M NaI + 0.05M I_2) and ferri/ferro cyanide (by mixing 0.05M $K_3[Fe(CN)_6]$ + 0.05M $K_4[Fe(CN)_6]$ + 1 M KCl electrolyte respectively.

The schematic diagram of experimental set up for studying the effect of intensity of illumination is shown in Fig.9.1. The crystal surfaces of photoelectrodes were illuminated by an incandescent lamp for photovoltaic measurements. The incident light intensity was adjusted by changing the distance between PEC cell and light source. The intensity of illumination at the crystal surface was measured with Suryamapi (Central Electronics Ltd., India) and photovoltage and photocurrent were recorded by digital multimeters (Systronics 435, India and Agronic 67, India).

9.3. RESULTS AND DISCUSSIONS :

When the semiconductor-electrolyte junction is illuminated with light having energy greater than band gap of semiconductor, electron-hole pairs are produced in the depletion region of junction and charge seperation takes place due to the local field present at the interface. When a counter electrode is immersed in the electrolyte and connected to the semiconductor, the photogenerated electron moves into the bulk of the semiconductor and through external circuit it reaches the counter electrode to reduce the oxidised species in the electrolyte. The hole is pushed to the electrode surface where it oxidizes the reduced species in the electrolyte.

The effect of intensity of illumination on the photocurrent density (J) - Voltage (V) characteristics with n-WSe_2 and p-WSe_2 electrodes are illustrated in Fig.9.2.(a,b and c) and Fig. 9.3. respectively. These figures show that the photocurrent density - voltage curves shift outwards with the increasing light intensity. Inorder to study the nature of variation of short circuit current ($I_{s.c.}$), open circuit voltage ($V_{o.c}$) wth respect to incident illumination (I) and for evaluation of the ideality factor (n) of illuminated junctions, semiconductor electrodes of n and p-type WSe_2 have been used. The results for n-type are shown in Fig.9.4 (a,b and c) while Fig. 9.5 shows the results for p-type photo-electrodes. It is observed that in the case of n-type electrodes the plots of short circuit currents versus light intensity are linear for all the electrodes, up to a certain value after which they deviate from the linarity. Where as in the case of p-type materials the behaviour is perfectly linear with increase in intensity. However, the open circuit voltage ($V_{o.c}$) is linear function of logarithem of incident light intensity (Fig.9.4 (a,b and c) and Fig. 9.5) for all the electrodes irrespective of the semiconducting nature i.e. n-type or p-type.

The non-linear dependence of $I_{s.c.}$ demontrates that the re-combination of photogenerated carriers at the semiconductor-electrolyte interface is limiting the rate of overall charge transfer reaction over the range of light intensities employed. According to kline etal (1) and Bicelli etal (2) the observed deviation from linearity of short circuit currents with respect to incident light intensity could mainly be attributed to the existence of numerous recombination centres. The recombination centres associated with samples having surface steps results in a lower quantum yield (3-5) at low intensity and limit the photocurrent at higher intensity. Bulk and space charge layer recombinations are also mechanisms which account for deviation from linearity (5). All these facts are supported from the observation that n-type surfaces are generally stepped.

The linear behaviour observed in the case of p-type materials can be attributed to the smoothness of their surfaces. Plots of $V_{o.c.}$ versus log I have been used to determine the junction ideality factor 'n' for both the n and p-type semiconductor electrodes.

According to Rajeshwar etal (6), if the semiconductor-electrolyte interface is modelled as a schottky barrier, then, it is possible to represent the current-voltage characteristics by the experession (7).

$$J = J_{ph} - J_d = J_{ph} - J_o \left[\exp(qv/kT)-1\right] \quad .....(9.1)$$

Here, J is the net current density, J_{ph} and J_d are the photocurrent density and darkcurrent density, respectively, J_o is the reverse saturation current density, V is the voltage, n is the "junction ideality" factor, and other terms have their usual significance. For bias voltages exceeding 3KT/q, we can neglect the last term in the bracket in equation (9.1). Also at equilibrium (open-circuit conditions), $J_{ph} = J_d$ and $V = V_{o.c}$ so that rearrangement of equation (9.1) yields

$$V_{o.c.} \cong \frac{n\,KT}{q} \ln \left(J_{sc}/J_o\right) \quad \text{.....(9.2)}$$

where $V_{o.c}$ is the open - circuit voltage and $J_{s.c}$ is the short circuit current density. If we further assume that $J_{sc} \propto I$ (= incident light intensity) and $J_{sc} >> Jo$, equation (9.2) reduces to the following expression.

$$V_{o.c.} \propto \frac{nKT}{q} \ln I \quad \text{.........(9.3)}$$

A plot of $V_{o.c}$ against lnI should yield a straight line from which values of 'n' may be determined for the particular device. Values of 'n' obtained from plots of $V_{o.c}$ versus ln I (Fig. 9.6 (a,b,c) and Fig 9.7) in the case of n and p-type solar cells are shown in Table 9.1.

It is seen that crystals grown by $TeCl_4$, $SeCl_4$+Se and $SeCl_4$ have their n values nearly equal to unity while in the case of Br_2 the value is much more than 1 (one) but it is still lessthan 2 (two). The ideal device has an n, value equal to unity. This shows that crystals grown by $TeCl_4$, $SeCl_4$+Se and $SeCl_4$ behave as ideal devices.

The higher values of n observed in the case of Br_2 point out that the recombination process in this case involve photogenerated electron-hole pairs either at semiconductor surface or in the depletion region (8). The recombination process cause a deviation from the ideal current voltage characteristics.

The effect of light intensity on the light to electrical convertion efficiency and fill factor for all the WSe_2 electrodes are given in Fig. 9.8(a,b,c) for n-type and Fig.9.9 for p-type. The decrease in efficiency in all the samples at higher light intensities can be attributed to the loss of fill factor and short circuit currents. According to Russak etal (9) the reduction in fill factor with increasing light intensity can be due to recombination at grain boundary or defect free sites in the space charge layer which becomes more pronounced with higher photon flux near the maximum power point. The flattening of bands (conduction and valence) as a result of high intensity of illumination reduces the space charge and efficiency of charge carrier seperation. Insufficient seperation of charge increases the recombination of photogenerated carriers. Which may ultimately lead to a reduction in efficiency.

Thus there is a decrease in efficiency with higher intensity of light used to illuminate the sample.

9.4. CONCLUSIONS :

1. The photocurrent density (J) - voltage curves shift outwards withincrease in intensity of illumination.
2. The open circuit voltages ($V_{o.c}$) are linear functions of logarithems of incident light intensity, for both n and p-type photoelectrodes.
3. In the case of n-type electrodes the short circuit currents are linear with the increase in illumination intensity upto a certain value after which they deviate from linearity, while in the case of p-type electrodes they remain linear.
4. The efficiency and fill factor decrease with increase in intensity of illumination.
5. The higher efficiencies (8.26%) have been observed for n-type WSe_2 electrodes (crystals grown by Br_2) and (9.05%) for p-type WSe_2 (crystals grown by $SeCl_4$) photoelectrodes at 10 mw/Cm^2 (intensity of illumination).
6. The n-type photoelectrodes (crystals grown by $TeCl_4$ and $SeCl_4$ + Se) show lower efficiency, which may be due to their surface morphology. This aspect will be discussed in detail in the next chapter.

TABLE 9.1.

JUNCTION IDEALITY FACTORS FOR ILLUMINATED TUNGSTEN DISELENIDE-ELECTROLYTE INTERFACE

WSe_2 grown by	Ideality factor calculated 'n'
$SeCl_4$	1.14
Br_2	1.75
$TeCl_4$	1.01
$SeCl_4$ + Se	1.07

R E F E R E N C E S

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CAPTIONS OF THE FIGURES :

Fig.9.1. Schematic diagram of experimental set up for studying the effect of illumination.

Fig.9.2.(a,b,c) photocurrent density (J) -Voltage(V) characteristics at different intensities of illumination of n-WSe_2 photoelectrodes.

Fig.9.3. photocurrent density (J)-Voltage (V) characteristics of different intensities of illumination of p-WSe_2 photoelectrode.

Fig.9.4(a,b,c) plots of open circuit voltage ($V_{o.c}$) and short circuit current ($I_{s.c}$) as a function of light intensity (I) for n-type electrodes.

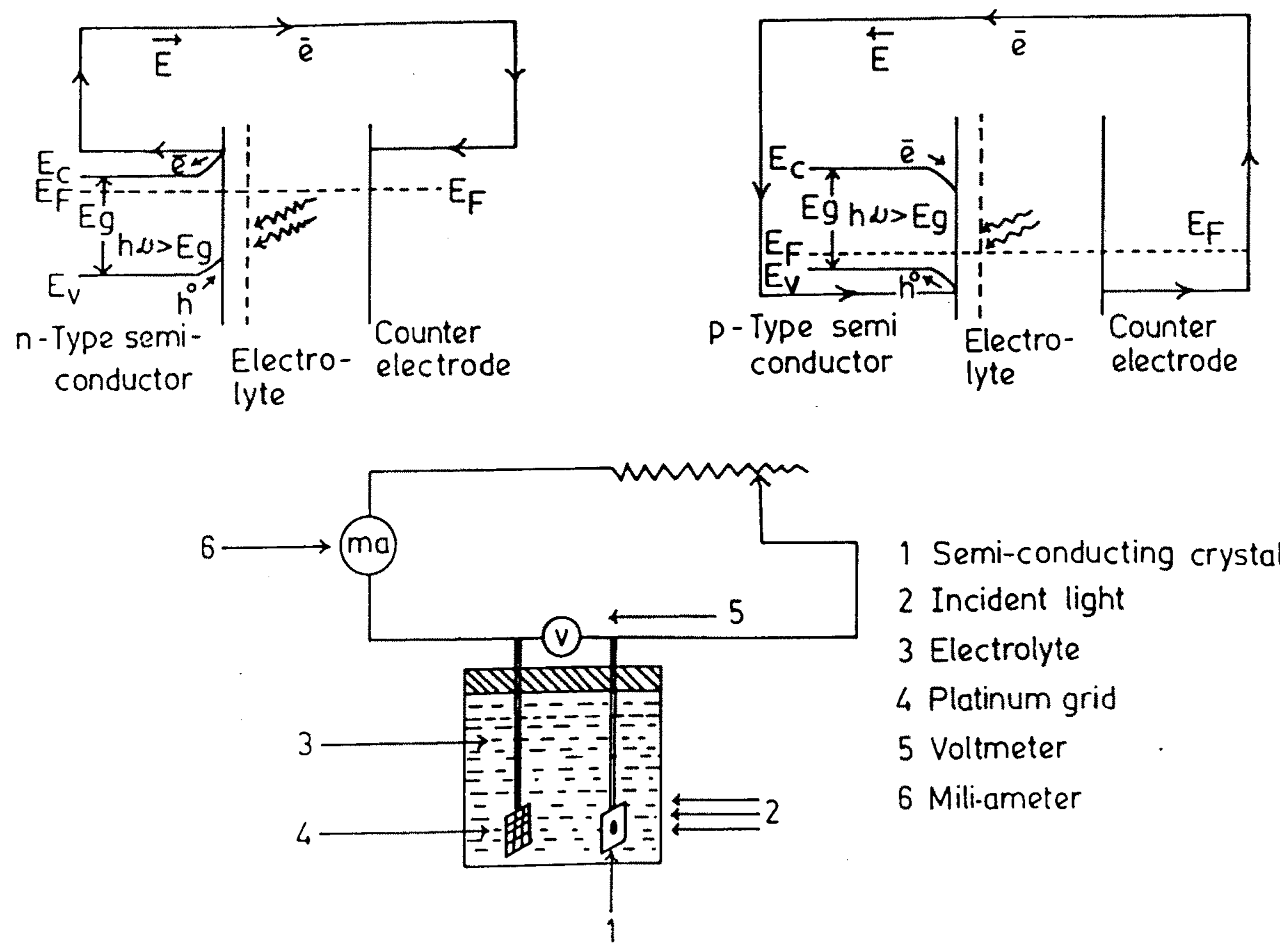
Fig.9.5. plot of open circuit voltage ($V_{o.c}$) and short circuit current ($I_{s.c}$) as a function of light intensity (I) for p-type electrode.

Fig.9.6.(a,b,c) plots of open circuit Voltage ($V_{o.c}$) as a function of logarithem of light intensity (lnI) for n-type electrodes.

Fig.9.7. plot of open circuit voltage($V_{o.c}$) as a function of logarithem of light intensity (lnI) for p-type electrode.

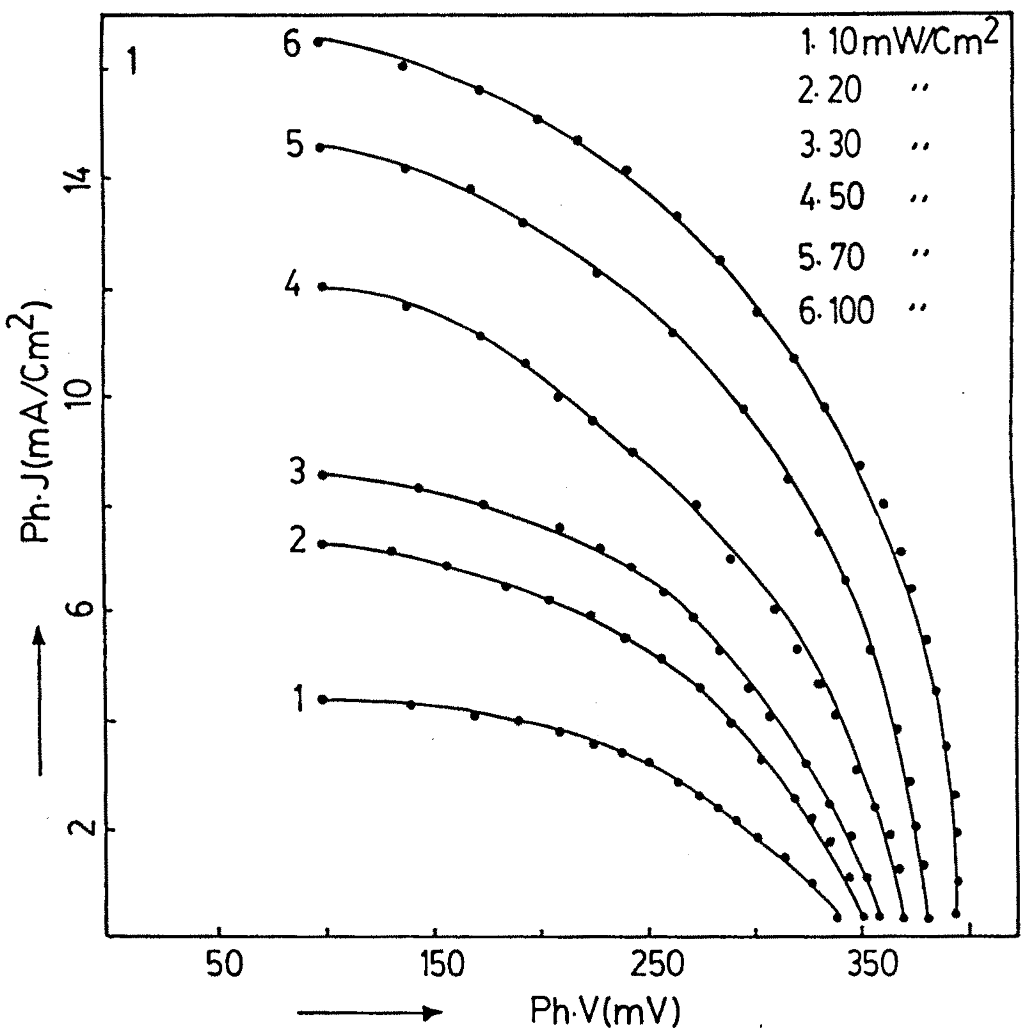
Fig.9.8.(a,b,c) plots of light to electrical conversion efficiency (η%) and fill factor (F.F.) as a function of light intensity (I) for n-WSe_2 electrodes.

Fig.9.9. plot of light to electrical conversion efficiency (η%) and fill factor (F.F.) as a function of light intensity for p-type WSe_2 electrode.



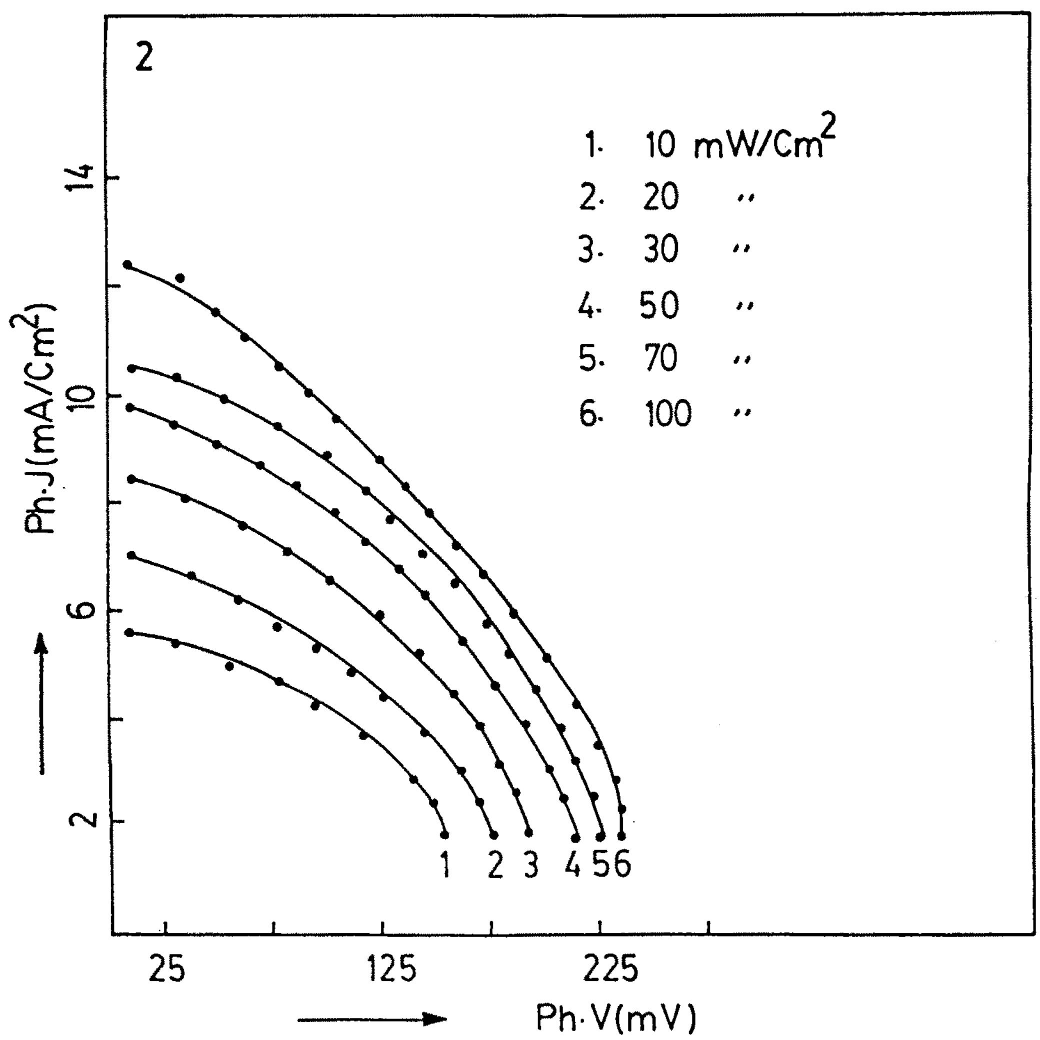
E
ē
Ec
EF
Eg
hν>Eg
Ev
h°
n-Type semi-conductor
Electro-lyte
Counter electrode
p-Type semi conductor
6
ma
V
5
3
4
2
1
1 Semi-conducting crystal
2 Incident light
3 Electrolyte
4 Platinum grid
5 Voltmeter
6 Mili-ameter

FIG. 9.1

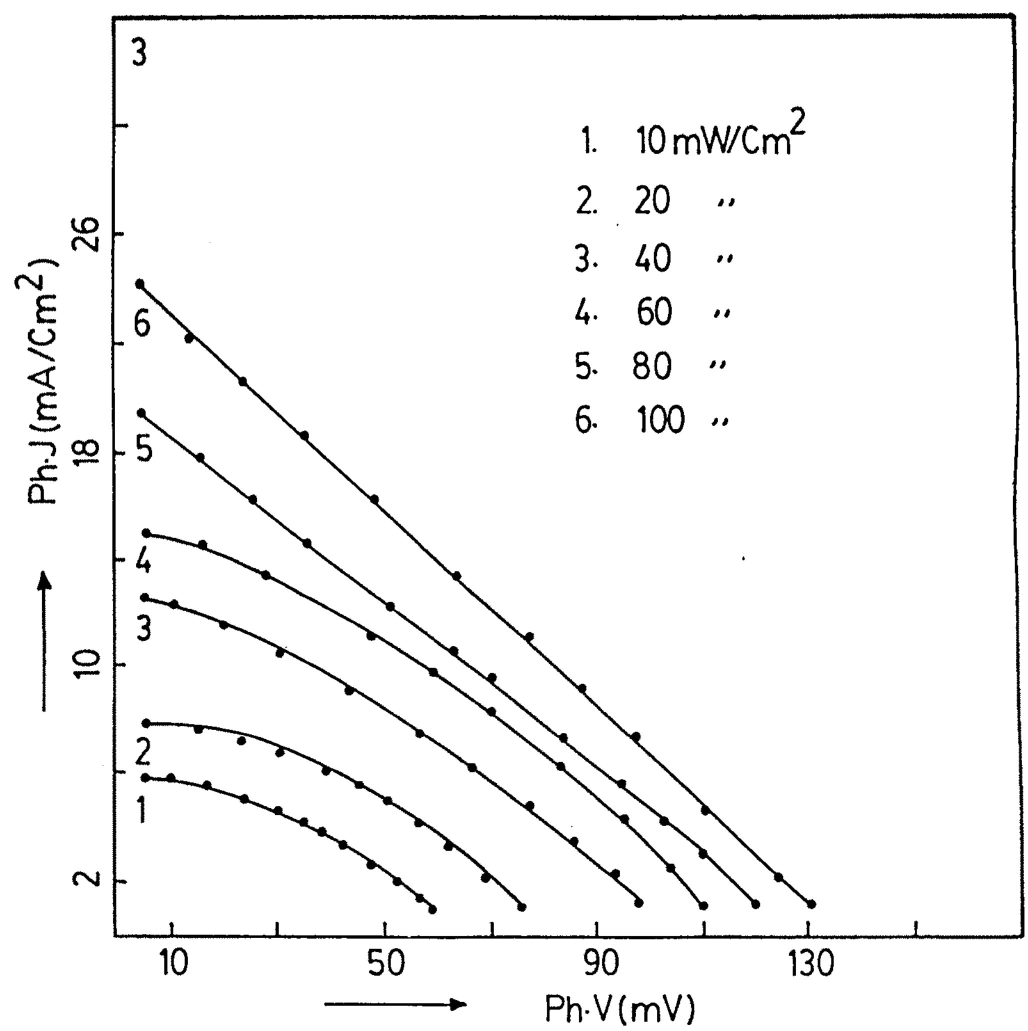


1· 10mW/Cm^2
2· 20 ''
3· 30 ''
4· 50 ''
5· 70 ''
6· 100 ''
Ph·J(mA/Cm^2)
Ph·V(mV)
2
6
10
14
50
150
250
350
1
2
3
4
5
6

FIG.9.2(a)

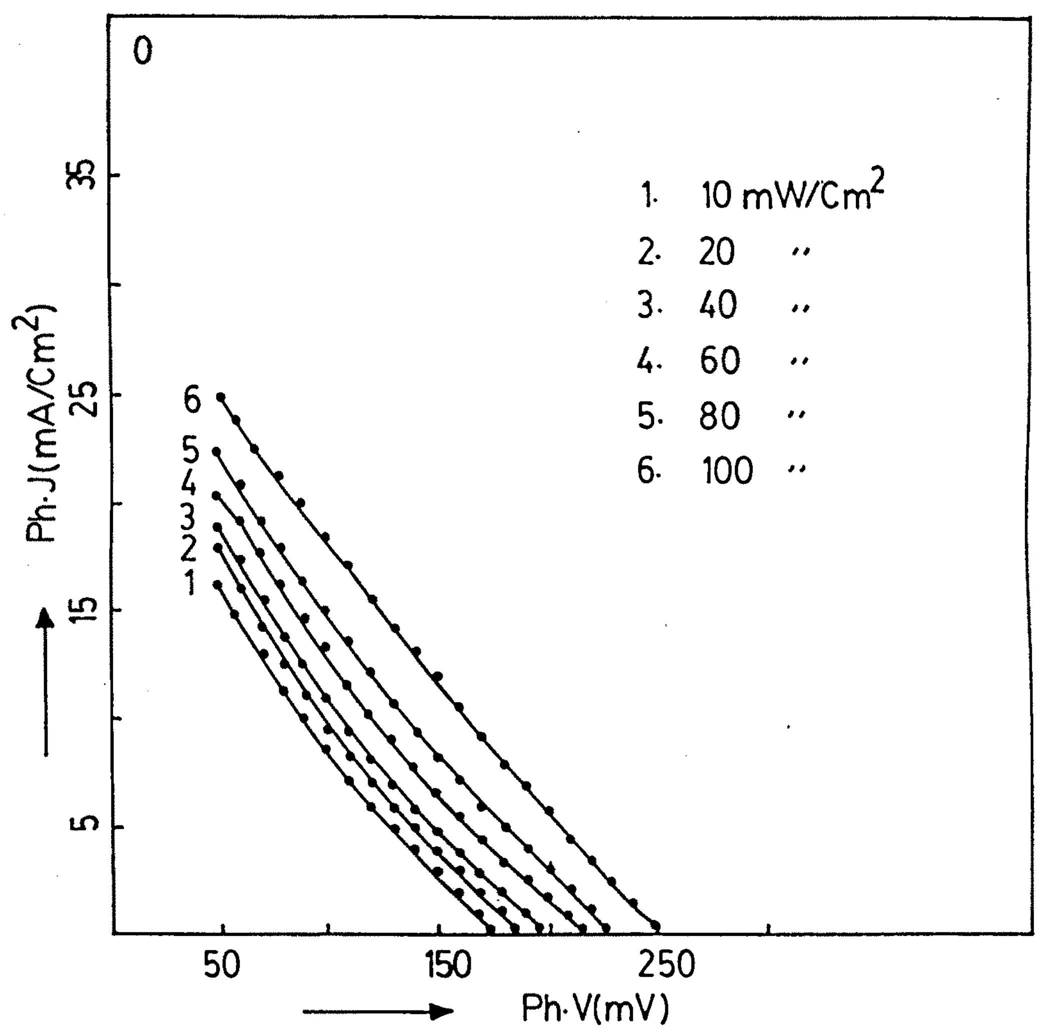

2
1. 10 mW/Cm2
2. 20 ,,
3. 30 ,,
4. 50 ,,
5. 70 ,,
6. 100 ,,
Ph·J(mA/Cm2)
14
10
6
2
1 2 3 4 5 6
25
125
225
Ph·V(mV)

FIG·9·2 (b)



3
1. 10 mW/Cm2
2. 20 ,,
3. 40 ,,
4. 60 ,,
5. 80 ,,
6. 100 ,,
Ph·J (mA/Cm2)
26
18
10
2
6
5
4
3
2
1
10
50
90
130
Ph·V (mV)

FIG·9·2 (C)



0
1. 10 mW/Cm²
2. 20 ''
3. 40 ''
4. 60 ''
5. 80 ''
6. 100 ''
Ph·J (mA/Cm²)
35
25
15
5
50
150
250
Ph·V(mV)

FIG-9.3

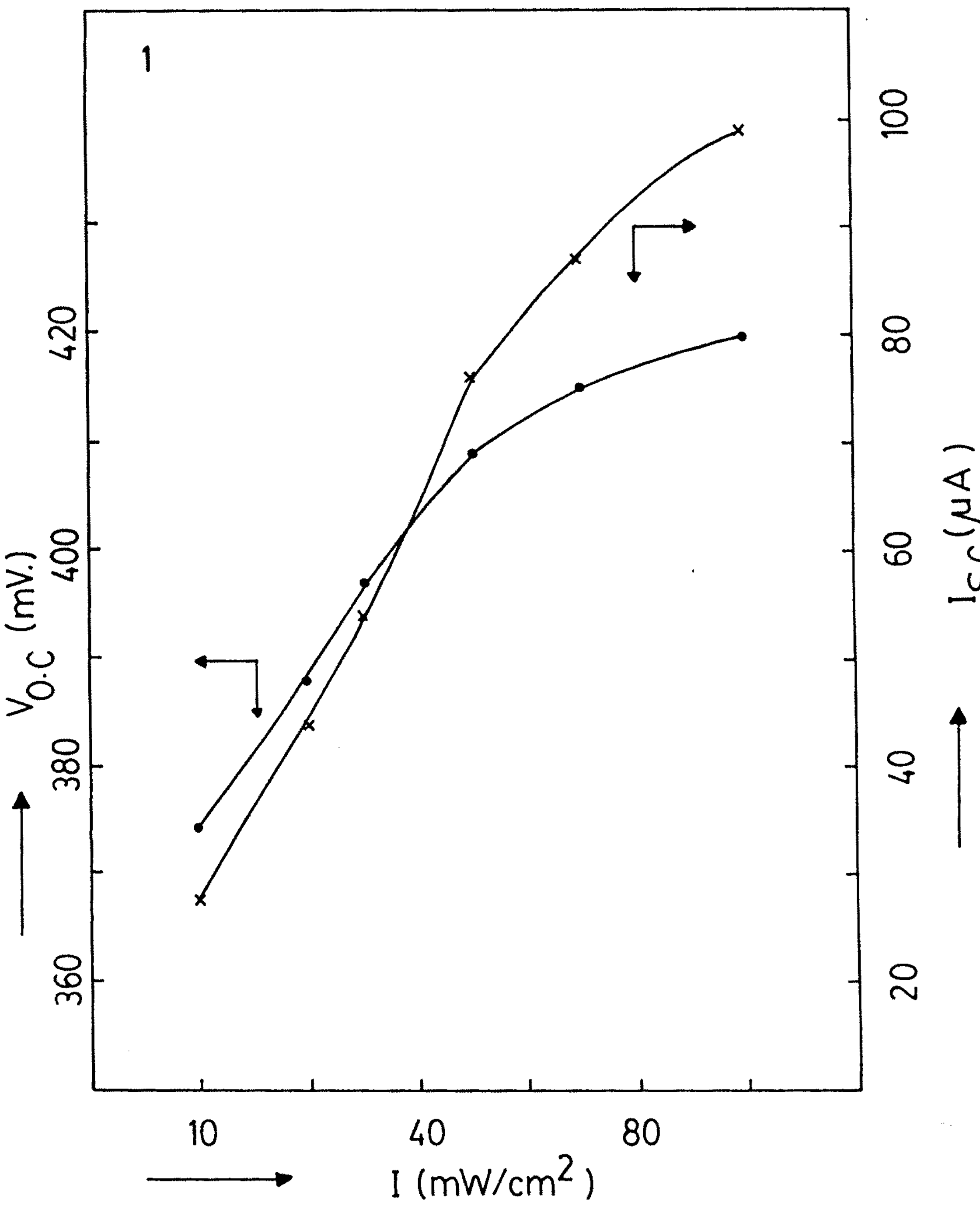


FIG. 9.4(a)

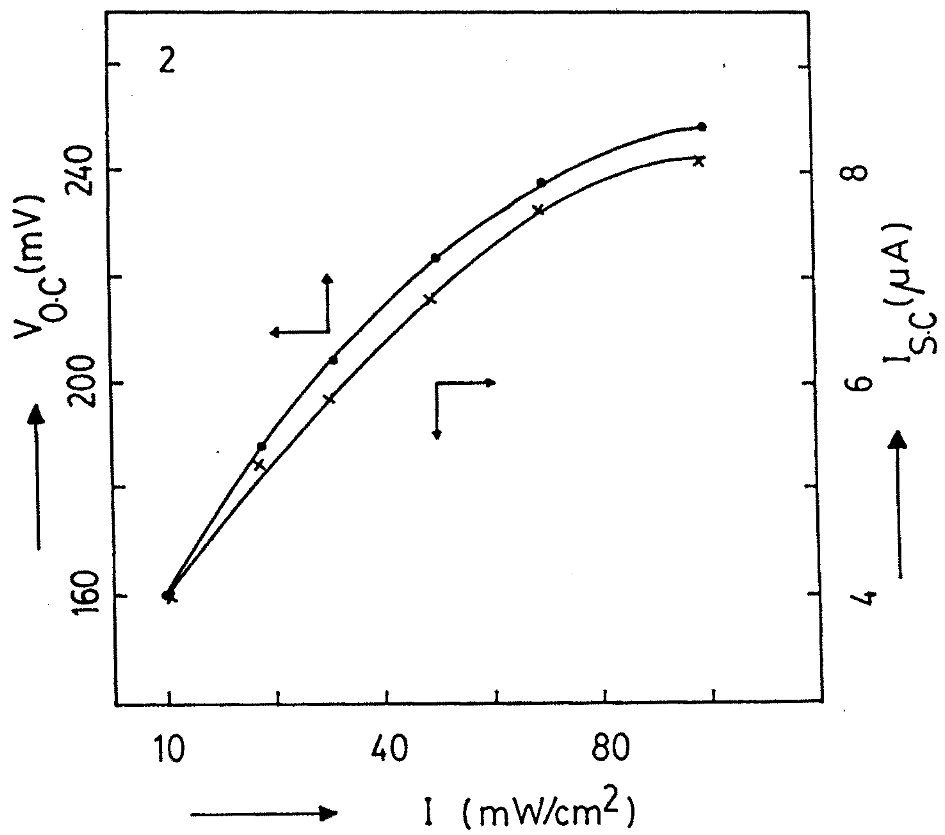


FIG. 9·4(b)

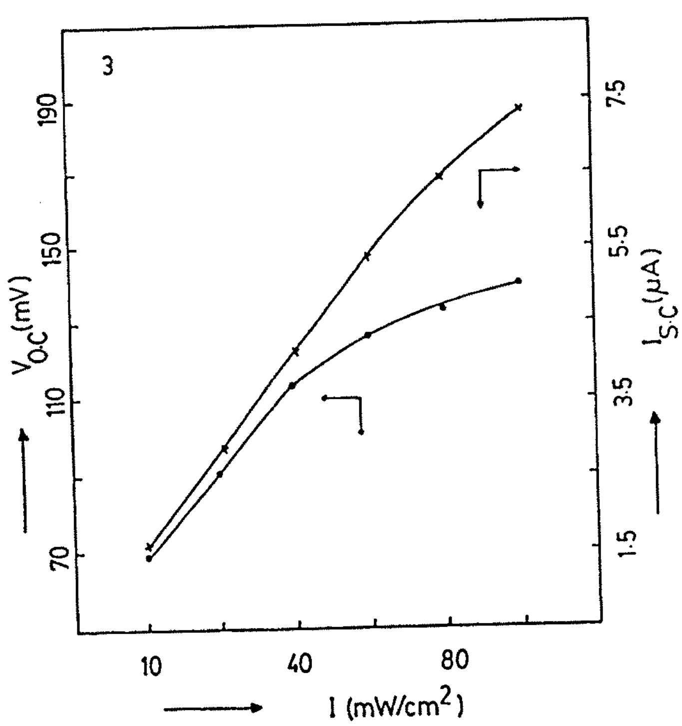


FIG. 9·4(c)

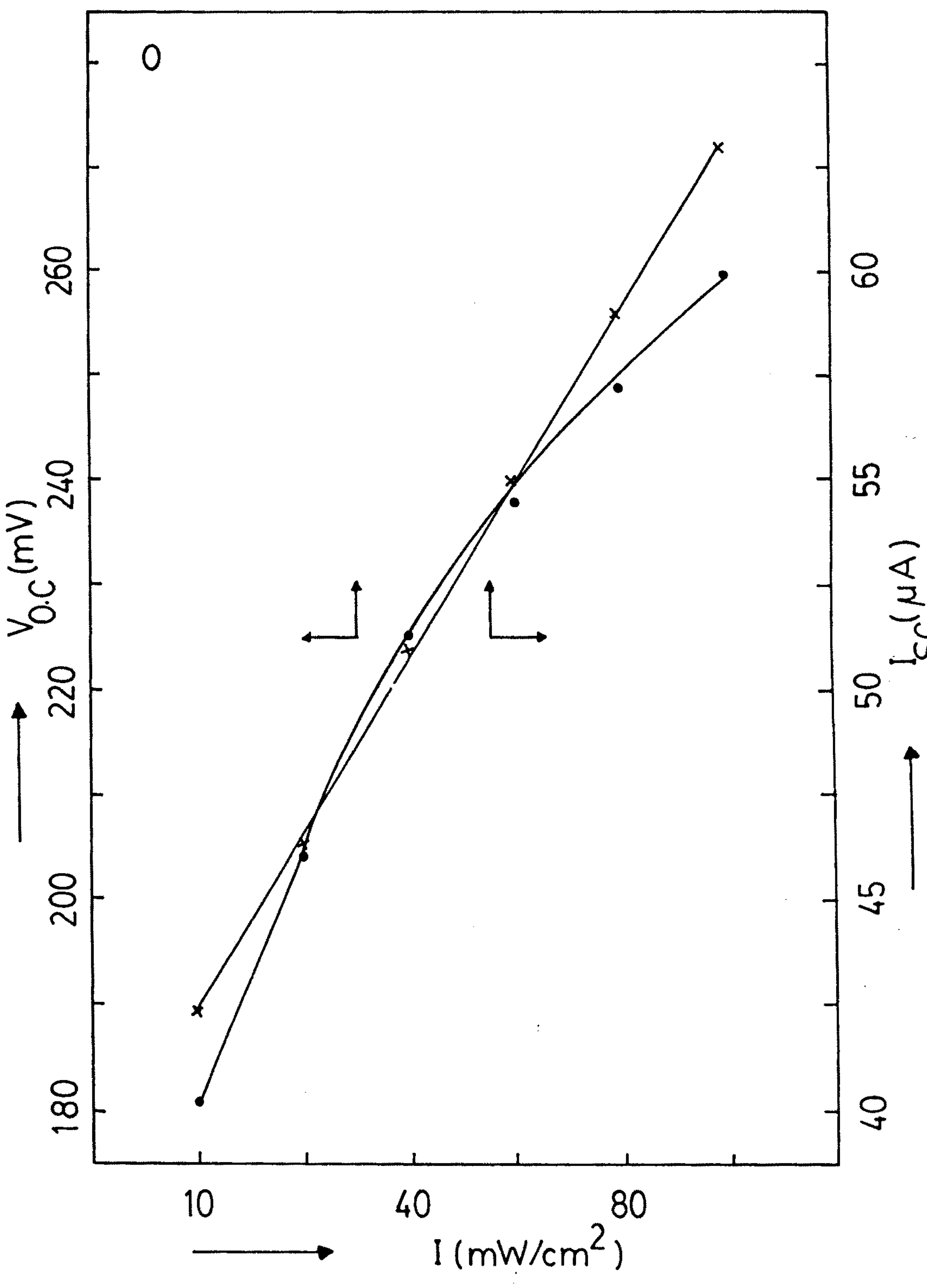


FIG.9.5

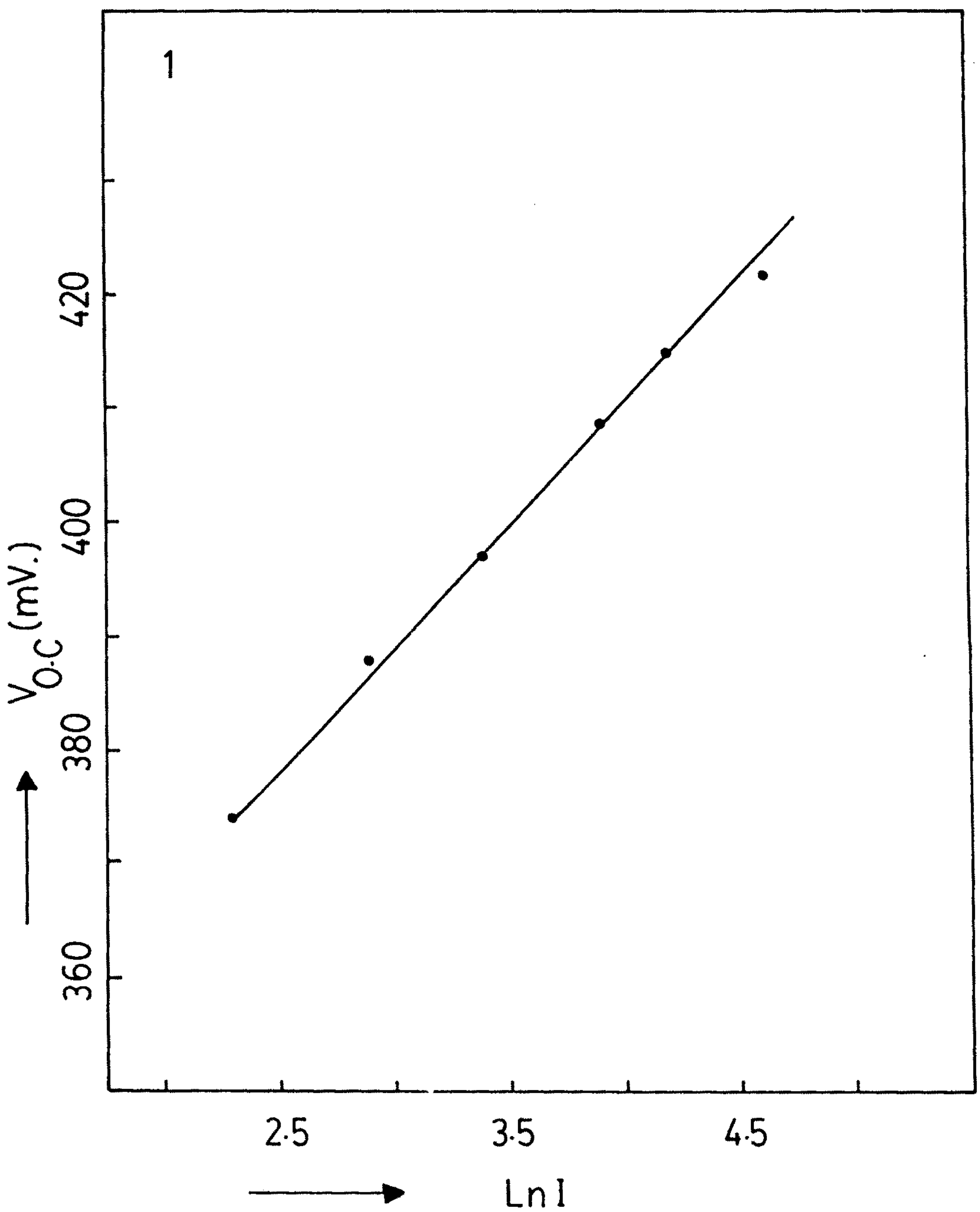


FIG. 9.6(a)

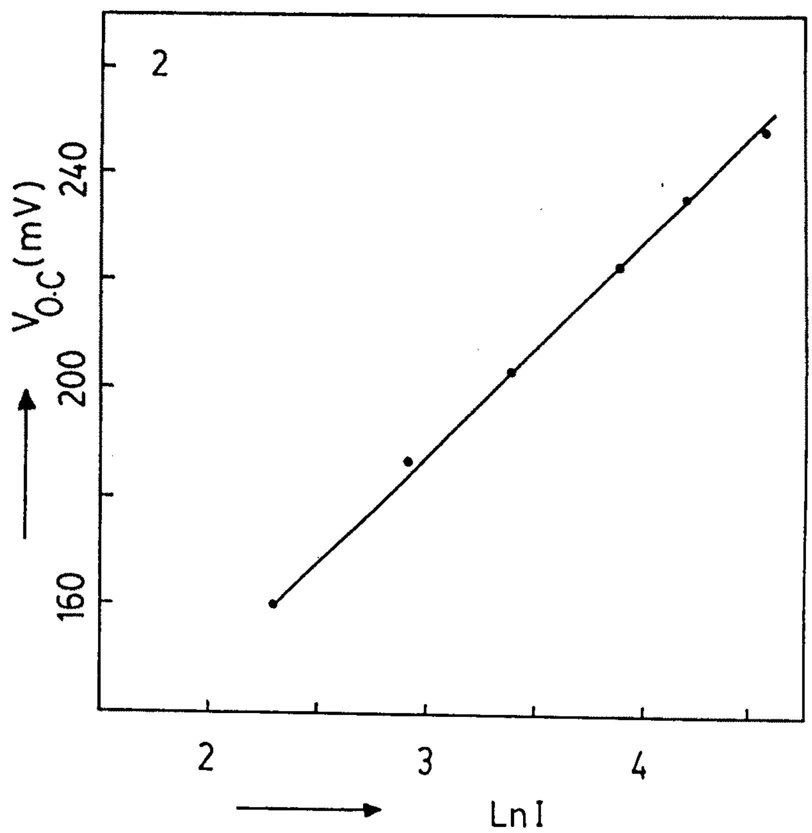


FIG. 9.6(b)

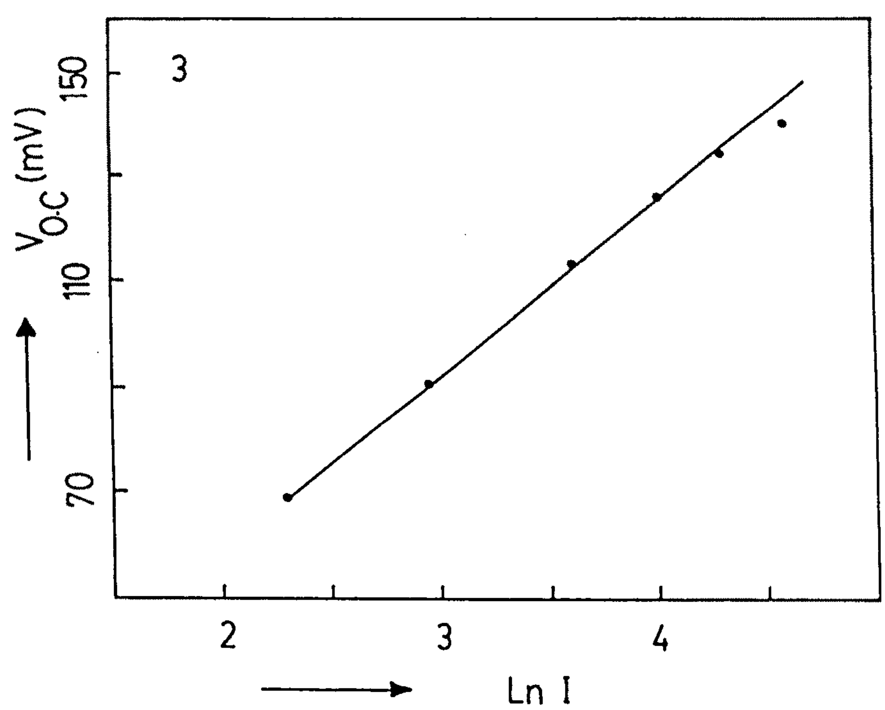


FIG. 9.6(c)

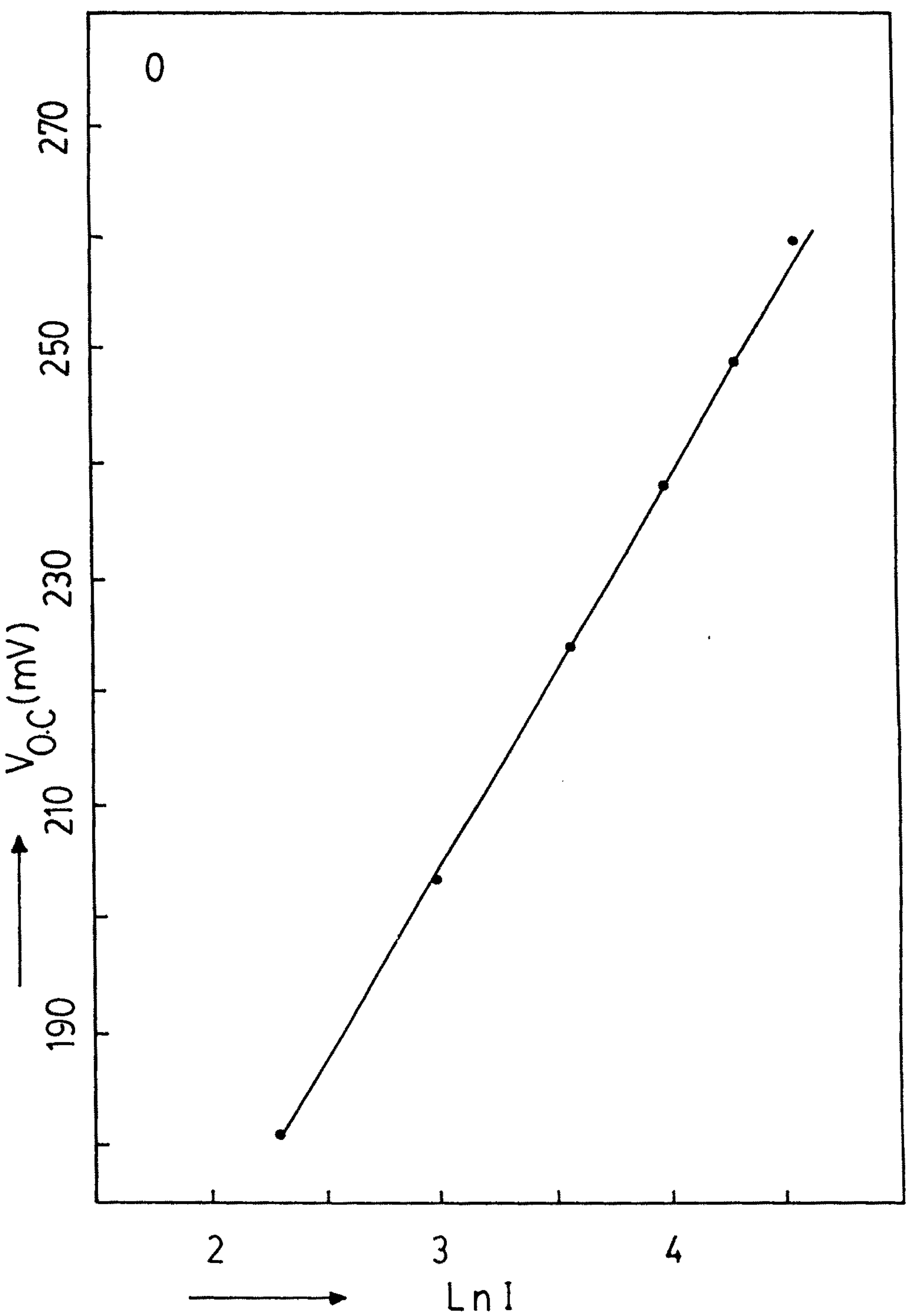


FIG. 9.7

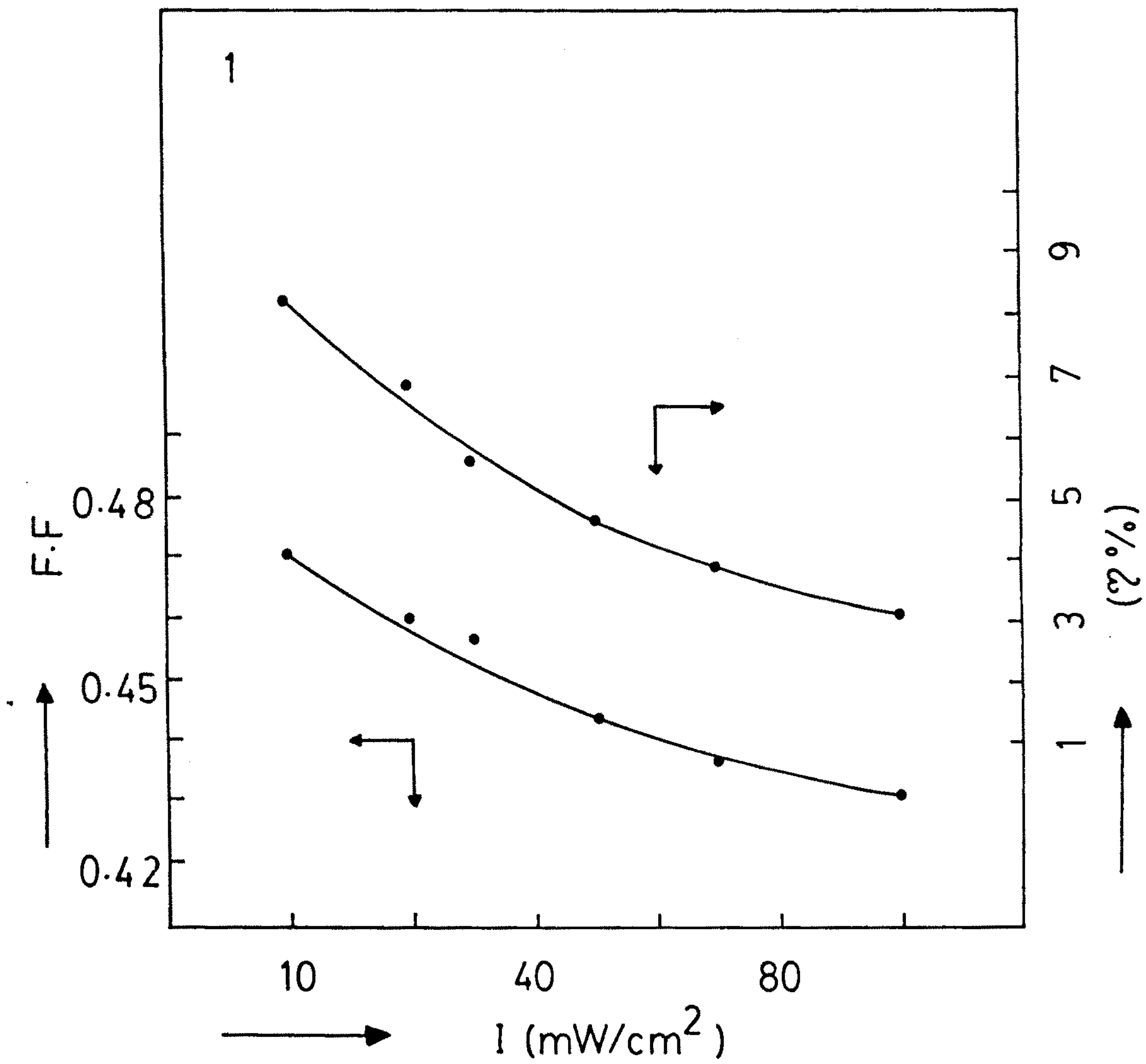


FIG. 9.8(a)

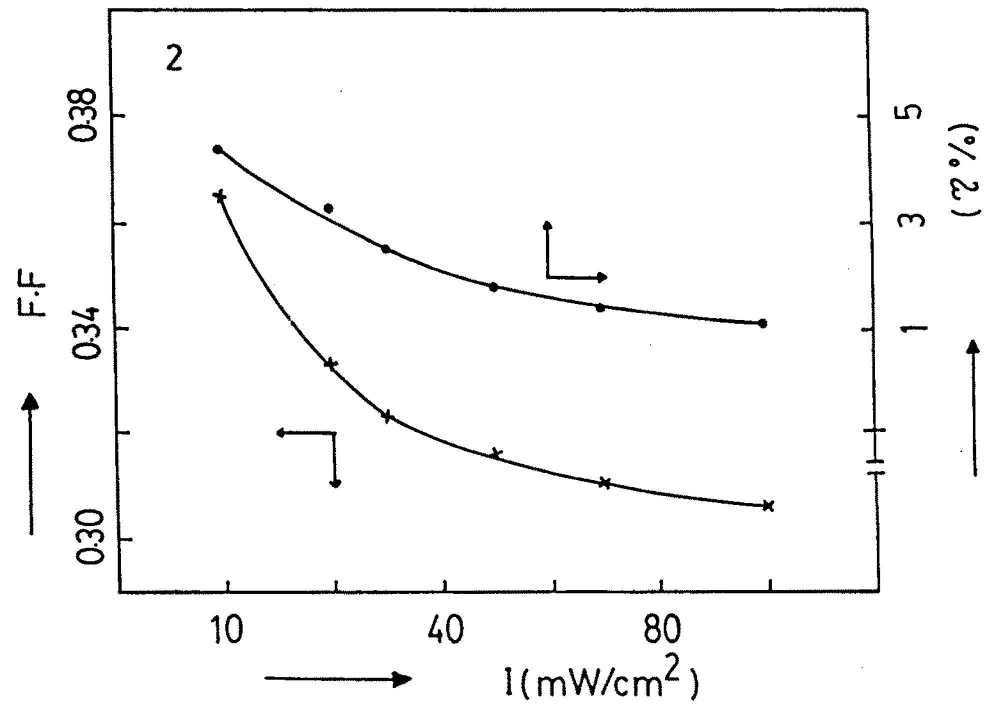


FIG. 9.8(b)

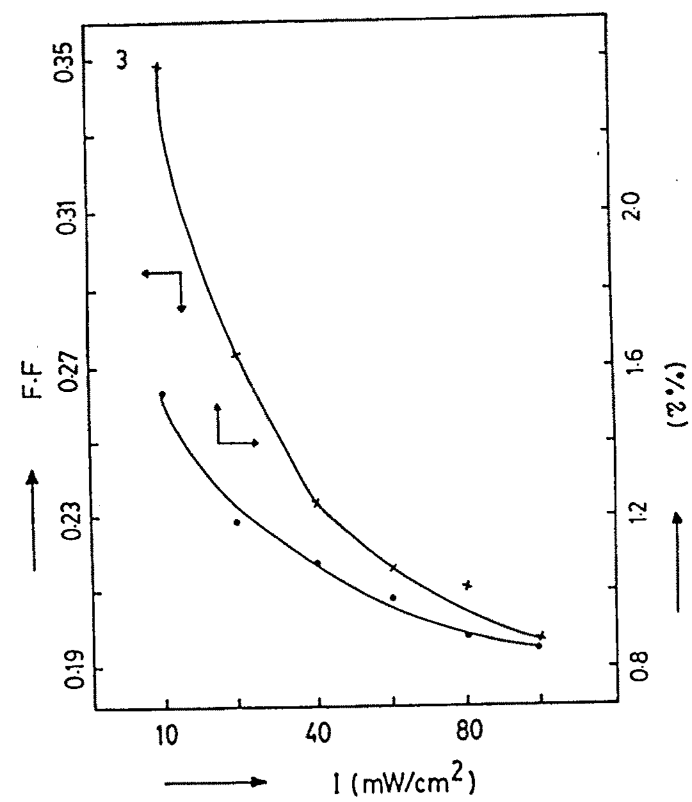


FIG. 9.8(c)

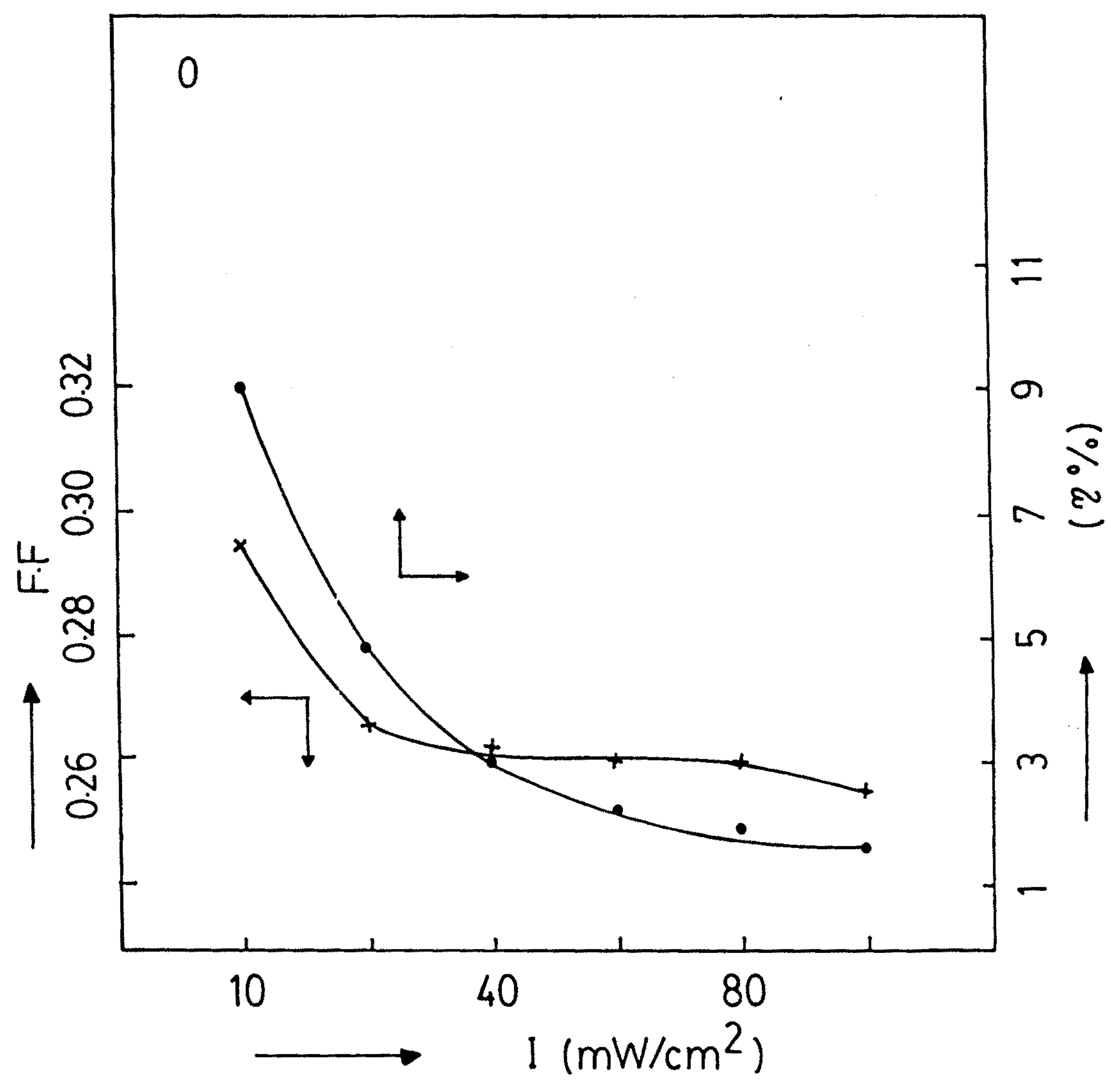


FIG. 9.9