

## Diffusion Length Measurements in CdS and CdSe Schottky Barrier Junctions (\*).

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(ricevuto il 27 Giugno 1980; manoscritto revisionato ricevuto il 7 Ottobre 1980)

**Summary.** — The minority carrier diffusion length has been measured on CdS and CdSe single crystals by means of the surface photovoltage method. By illuminating the samples through semi-transparent metal semiconductor Schottky barriers and for a given photovoltage signal, a linear relation was found between the intensity of light and the absorption length. By extrapolating to zero light intensity such a straight line, the diffusion length was obtained as the intercept with the  $x$ -axis. For good accuracy, a least-square fit method was employed to calculate the diffusion length values. The agreement of measurements performed on some Schottky diodes prepared in different ways and displaying different spectral responses confirmed a near independence of the SPV technique on some material parameters and experimental conditions.

### 1. — Introduction.

The minority carrier diffusion length  $L$  is a basic material property for characterizing semiconductor materials and evaluating their possibility to be used as electronic devices. Generally, the determination of  $L$  employs the measurement of the minority carrier lifetime  $\tau$ ; thus the diffusion length is calculated by means of the well-known relation  $L = (D\tau)^{\frac{1}{2}} = (\mu(kT/e)\tau)^{\frac{1}{2}}$ , where  $D$  and  $\mu$  are, respectively, the diffusion constant and the mobility of the minority carriers. Thus  $L$  and  $\tau$  measurements are considered as being synonymous. However, it should be kept in mind that  $\tau$ , the minority carrier

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(\*) To speed up publication, the authors of this paper have agreed to not receive the proofs for correction.

mobility, could be different from the value achieved in the majority carrier situation due to the screening effect of the majority carriers <sup>(1)</sup>. From this point of view, the use of experimental methods by which  $L$  can be directly measured seems more available. In the past years, many techniques have been developed to measure the value of the minority carrier diffusion length in semiconductors. Most of the measurements employed photons as the means of exciting excess carriers, even though excitation by nuclear radiation <sup>(2,3)</sup>, charged particles <sup>(4)</sup> and electron beam <sup>(5)</sup> have also been used. Probably, the most simple experimental method consists in the collection of the excess carriers, which are photogenerated from a light with an appropriate wavelength, by means of  $p$ - $n$  or Schottky junctions. By the diffusion equation with some boundary conditions it is possible to describe the excess carrier distribution.

From this, it results that the diffusion length value can be obtained by measuring the induced current or voltage as a function of appropriate parameters.

The use of  $p$ - $n$  junctions involves contributions to the photocurrent due to both sides of the heterojunction. Thus it is preferable to use Schottky barriers by exciting the surface of the semiconductor through the semi-transparent metal layer, or by directly illuminating the surface of the narrow band gap material of an heterojunction by virtue of the window effect.

The minority carrier diffusion length has been investigated in bulk semiconductors, epitaxial layers and diffusion  $p$ - $n$  junctions by measuring the surface photovoltage as a function of the incident light intensity. If some appropriate conditions are fulfilled, this approach, which is known as surface photovoltage method (SPV), allows one to obtain a linear relation between light intensity and absorption length. By extrapolating to zero light intensity,  $L$  results as the  $x$ -axis intercept.

Recently, this technique has been proposed as a suitable one for process control of finished solar cells because  $L$  is measured in a nondestructive way giving also some information about the process influence on the starting material <sup>(6,7)</sup>. As has been previously reported, we used this technique to measure the electron diffusion length in  $n$ -Zn<sub>x</sub>Cd<sub>1-x</sub>S/ $p$ -GaAs heterojunction solar cells <sup>(8)</sup> and in ZnSe semi-transparent Schottky barrier <sup>(9)</sup>.

<sup>(1)</sup> J. P. BLOOD and F. W. ORTON: *Rep. Prog. Phys.*, **41**, 157 (1978).

<sup>(2)</sup> L. W. ANKERMAN, M. F. MILLEA and M. MCCOLL: *J. Appl. Phys.*, **38**, 685 (1967).

<sup>(3)</sup> R. GREMMELMAIER: *Proc. IRE*, **46**, 1045 (1958).

<sup>(4)</sup> W. VAN ROOSBROECK: *J. Appl. Phys.*, **26**, 380 (1955).

<sup>(5)</sup> C. J. WU and D. S. WITTRY: *J. Appl. Phys.*, **49**, 2877 (1978).

<sup>(6)</sup> E. D. STOKES and T. L. CHU: *Appl. Phys. Lett.*, **30**, 425 (1978).

<sup>(7)</sup> T. L. CHU, E. D. STOKES and S. S. CHU: *Solar Cells*, **1**, 222 (1979/80).

<sup>(8)</sup> L. TARRICONE and E. GOMBIA: *Solar Energy Materials*, **2**, 45 (1979).

<sup>(9)</sup> S. MORA, N. ROMEO and L. TARRICONE: *Solid State Commun.*, **33**, 1147 (1980).

In this paper such an investigation has been extended to  $n$ -CdS and  $n$ -CdSe single crystals by employing Schottky barrier diodes.

## 2. - Experimental details.

Single crystals of  $n$ -CdS and  $n$ -CdSe were investigated. The CdS crystals were prepared from the vapour phase by the Piper-Polich method and (0001) oriented. The resistivity of CdS samples was about  $0.1 \Omega \cdot \text{cm}$  with an Hall mobility of about  $60 \text{ cm}^2 \text{ V}^{-1} \text{ s}$  as measured by good Ohmic indium contacts. The carrier concentration was calculated to be  $n \simeq 10^{18} \text{ cm}^{-3}$ . One surface of the monocrystalline slices of CdS was roughly lapped with a diamond paste to gain a freshly damaged surface which generally allows one to obtain very good Ohmic contacts. Therefore, indium was evaporated under high vacuum. The Schottky barriers were prepared in the following way: i) the surface was lapped and polished with a diamond paste up  $0.2 \mu\text{m}$  in size; ii) after having masked the surface with the Ohmic contact, the sample was etched in  $\text{Br} + \text{methanol } 10\%$  solution for a few minutes to remove the surface damage which was mechanically introduced; iii) after several rinsing steps, the crystal was placed under high vacuum where a thin gold contact ( $\sim 200 \text{ \AA}$ ) was evaporated at a pressure of about  $10^{-6}$  Torr.

The CdSe crystals were grown by vapour phase in a flow of argon. They showed a smooth surface which was mechanically polished with  $0.2 \mu\text{m}$  diamond paste. The Schottky contact was prepared in the same way as for CdS although some CdSe crystals have not been etched before the evaporation of the semi-transparent metal. The samples used for the measurements displayed a resistivity varying from  $0.6 \Omega \cdot \text{cm}$  to  $0.5 \cdot 10^2 \Omega \cdot \text{cm}$ . A Cary spectrophotometer was employed in order to obtain the absorption coefficient  $\alpha$  as a function of the wave-length. Some CdS and CdSe specimens have been carefully sharpened to achieve values of  $\alpha$  up to  $10^3 \text{ cm}^{-1}$ . The experimental set-up for the diffusion length measurements was the same used in previous works <sup>(8,9)</sup>.

## 3. - Theory.

The SPV method has been analysed in previous works <sup>(6,10,11)</sup>. In the first experiments, capacitive contacts were used to obtain a surface space charge region and under some particular assumptions the diffusion length  $L$  was determined by measuring the surface photovoltage as a function of the wave-length of the incident light. The basic theory assumes that the photovoltage

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<sup>(10)</sup> A. M. GOODMAN: *J. Appl. Phys.*, **32**, 2550 (1961).

<sup>(11)</sup> E. Y. WANG, C. R. BARAONA and H. W. BRONDHORST jr.: *J. Electron. Soc.*, **121**, 973 (1974).

can be expressed as a function of the excess minority carrier density  $\Delta p$  upon the condition that  $L$  and the absorption length  $\alpha^{-1}$  are much greater than the width  $W$  of the space charge region and much smaller than the thickness  $d$  of the samples (that is  $L \ll d$ ,  $1/\alpha \ll d$ ,  $L \gg W$ ,  $1/\alpha \gg W$ ). A light intensity  $I$ , which induces on the surface, creates an excess minority carrier density  $\Delta p$ , which can be expressed as

$$(1) \quad \Delta p = \frac{\gamma I (1 - R) \alpha L}{[D/L + s](1 + \alpha L)},$$

where  $\gamma$  is the quantum efficiency,  $R$  is the optical-reflection coefficient,  $D$  is the diffusion coefficient and  $s$  is the surface recombination velocity. Besides, by considering a low level of injection, neglecting trapping and recombination processes in the space charge region and assuming a small variation of quantum efficiency and reflectance with the wave-length, the incident-light intensity  $I$  which is required to achieve a given  $\Delta p$  value and then a given SPV signal becomes a linear function of the absorption length. After some manipulations from eq. (1) it follows that

$$(2) \quad I = C(\alpha^{-1} + L),$$

where  $C$  is a constant which depends on the given SPV signal. Thus, by extrapolating to zero light intensity the straight line according to eq. (2),  $L$  can be determined as the negative intercept at  $\alpha^{-1} = -L$ . The hypotheses which have been illustrated were verified both on CdS and CdSe diodes, as is displayed in table I, where the values of the parameters  $d$ ,  $\alpha^{-1}$ ,  $W$ ,  $L$  are reported. Moreover, in the experiments, a high degree of monochromaticity was required because of the rapid variation of the optical-absorption coefficient with

TABLE I.

Sample	$p$ ( $\Omega \cdot \text{cm}$ )	$n$ ( $\text{cm}^{-3}$ )	$\mu_n$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$d$ (cm)	$W$ (cm)
CdS	0.1	$\sim 10^{18}$	60	$3 \cdot 10^{-2}$	$10^{-5}$
nonetched 13-CdSe	$0.5 \cdot 10^2$	$\sim 10^{14}$	720 <sup>(12)</sup>	$2 \cdot 10^{-2}$	$3.5 \cdot 10^{-4}$
etched 14-CdSe	0.6	$\sim 10^{16}$	720 <sup>(12)</sup>	$2 \cdot 10^{-2}$	$3.8 \cdot 10^{-5}$

Sample	$L$ ( $\mu\text{m}$ )	$\gamma$ (s)	$\Delta\lambda$ ( $\text{\AA}$ )	$\Delta\alpha^{-1}$ ( $\mu\text{m}$ )
CdS	$0.25 \pm 0.05$	$\sim 1.7 \cdot 10^{-9}$	$5000 \div 5120$	$0.3 \div 4$
nonetched 13-CdSe	$4.59 \pm 1.01$	$\sim 1.0 \cdot 10^{-7}$	$7170 \div 7310$	$5 \div 100$
etched 14-CdSe	$4.98 \pm 0.34$	$\sim 1.3 \cdot 10^{-7}$	$7080 \div 7200$	$2 \div 15$

<sup>(12)</sup> A. N. GEORGIOBIANI: *Sov. Phys. Usp.*, **17**, 424 (1974).

the wave-length which is a typical characteristic of direct-gap material such as the II-VI compounds. Consequently any variation of the parameters  $\gamma$ ,  $R$  and  $s$  could be neglected.

#### 4. - Experimental results.

In fig. 1a), b) two forward and reverse  $J/V$  characteristics which have been obtained in Au/CdS and Au/CdSe Schottky diodes at room temperature and in the dark are represented. In the linear part of the characteristics, the quality factor  $n$  was calculated to be  $n = 2.4$  and  $n = 2.9$  for CdS and CdSe diodes, respectively. Values of  $n$  higher than 1 are generally ascribed to the presence

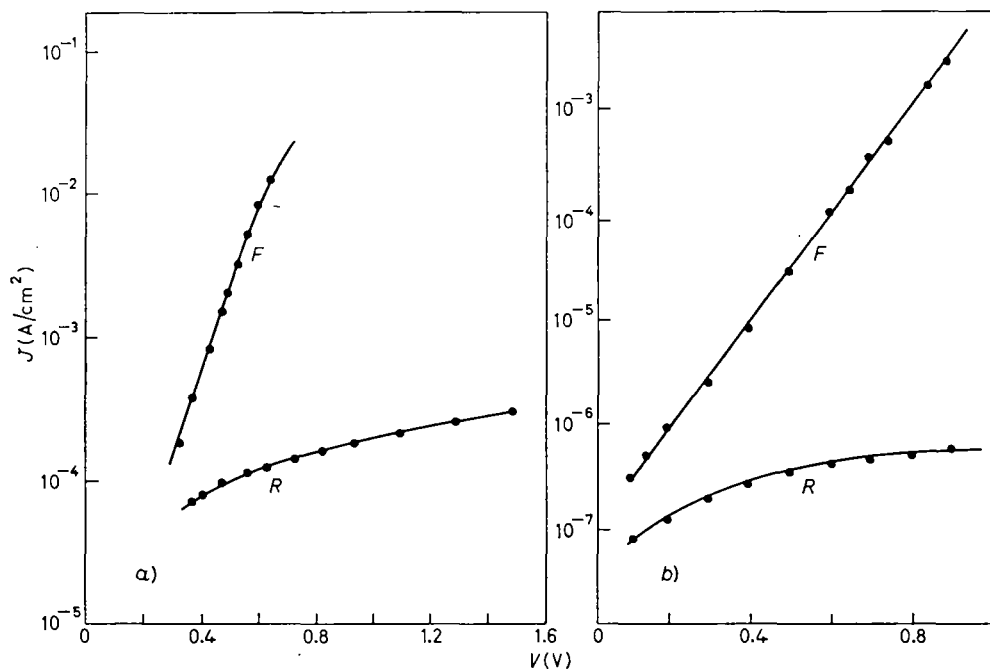


Fig. 1. - Forward and reverse  $J/V$  characteristics of b) Au/CdS and a) Au/CdSe at room temperature and in the dark.

of an insulating layer at the interface of the metal-semiconductor junction. Such an insulating layer could affect the given SPV signal. However, this fact causes only a change of the  $C$  constant in eq. (2), so that any influence on the diffusion length measurements can be neglected. In fig. 2, the values of light intensity in arbitrary units as a function of  $\alpha^{-1}$  for different open-circuit voltages for an Au/CdS diode are plotted. The experimental points, obtained by chopped light and lock-in detection, lie on straight lines. By a least-square fit method,

the value of  $L$  was obtained (table I). In fig. 3a), b) two similar curves relative to  $\Delta u/\text{CdSe}$  diodes are reported. Specimens with different properties have been used in this last case. In particular, they exhibited a different spectral response, as can be seen in fig. 4. Here the curves labelled 1) and 2) are relative to nonetched surface crystals with lower doping level and etched surface crystals with higher doping level, respectively.

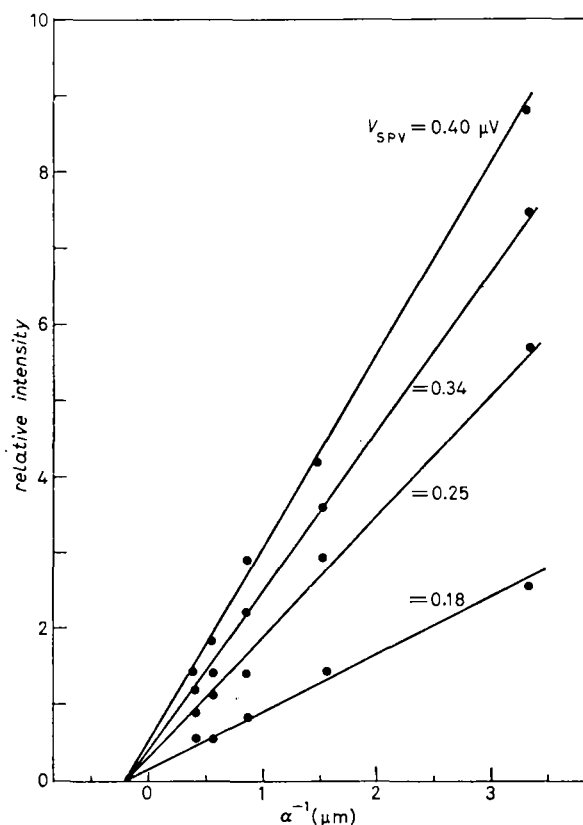


Fig. 2. — Relative light intensity vs. the inverse of the optical-absorption coefficient for a  $0.1 \Omega\cdot\text{cm}$  CdS Schottky junction.

As is already known, a higher impurity concentration causes a lower open-circuit photovoltage in Schottky barrier <sup>(13)</sup>. Moreover, the presence of a peak in the response of the nonetched samples, curve 1), which disappears in the response relative to the etched samples, curve 2), could be explained by taking into account a different influence of the surface recombination velocity. By

<sup>(13)</sup> H. J. HOVEL: in *Semiconductor and Semimetals*, Vol. **11**, *Solar Cells* (New York, N. Y., 1975), p. 123.

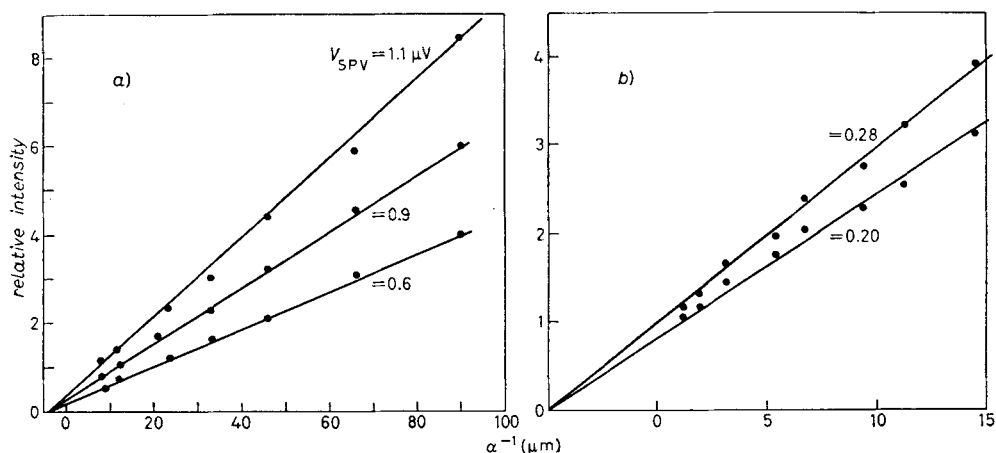


Fig. 3. — Relative light intensity *vs.* the inverse of the optical-absorption coefficient, respectively, for a)  $0.5 \cdot 10^3 \Omega \cdot \text{cm}$  and b)  $0.6 \Omega \cdot \text{cm}$  CdSe Schottky junctions. The measurements were performed on a) nonetched and b) etched crystalline surfaces, respectively.

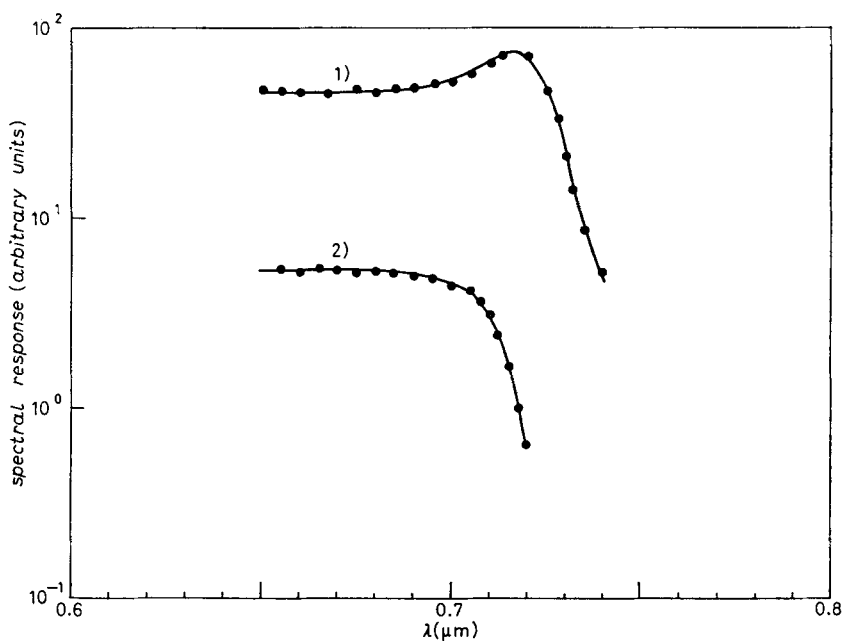


Fig. 4. — Spectral response of CdSe Schottky diodes. Curve 1) is relative to nonetched surfaces of specimens displaying a resistivity of  $0.5 \cdot 10^3 \Omega \cdot \text{cm}$  and an acceptor concentration of about  $10^{14} \text{ cm}^{-3}$ . Curve 2) is relative to etched surfaces of specimens displaying a resistivity of  $0.6 \Omega \cdot \text{cm}$  and an acceptor concentration of about  $10^{16} \text{ cm}^{-3}$ .

observing the low-energy behaviour of the curves drawn in fig. 4, one sees that two different spectral regions had to be used to achieve the diffusion length measurements. Notwithstanding this, the diffusion length value which was obtained in the same way as previously illustrated for CdS crystals, resulted to be about the same within the experimental errors, as is shown in table I. Here an evaluation of the corresponding minority carrier lifetimes has been attempted by using the mobility values parallel to the *c*-axis which are reported in the literature both for CdS and CdSe (<sup>12</sup>). The lifetime values are in agreement with the measurements reported in the case of CdS (<sup>14</sup>), while they are higher than the values which have been previously obtained for CdSe by PEM effect (<sup>15</sup>). This last disagreement could be due to a better quality of the CdSe crystals which have been investigated here. In fact, it is well known that the minority carrier lifetime can be influenced by the impurity concentration (<sup>16</sup>). For example, for CdS, for which values of  $\tau$  varying between  $10^{-7}$  and  $10^{-14}$  s are reported, the higher lifetime values were observed on higher-purity and higher-resistivity crystals (<sup>14</sup>).

## 5. - Conclusions.

The SPV method, extended to the case of Schottky junctions, was employed to measure the minority carrier diffusion length in CdS and CdSe crystals. By a least-square fit technique, the diffusion length values were obtained and a good accuracy was achieved also in the case of very short diffusion length ( $L < 0.5 \mu\text{m}$ ) as it has been measured in CdS samples. Such a low value, corresponding to a minority carrier lifetime of about  $\tau \simeq 1.7 \cdot 10^{-9}$  s, should be due to the high doping level ( $\sim 10^{18} \text{ cm}^{-3}$ ). In the case of CdSe, the specimens exhibited a different resistivity between them and a corresponding donor concentration always much lower than in the CdS crystals. Notwithstanding this, we obtained values of the diffusion length which within the experimental uncertainties were coincident. This can be better understood by taking into account that for lower concentrations the effect of the impurities on the carrier lifetime becomes less effective (<sup>16</sup>). Moreover, because of the higher self-compensation effect which is generally present in II-VI compounds, one should keep in mind that the value of the electrical resistivity cannot be considered as the most suitable parameter to correlate the diffusion length and the lifetime values with the crystal properties. In conclusion, the SPV method has shown to be a suitable technique to measure also very short values of  $L$ . The agreement of values achieved on samples prepared in different ways and displaying

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(<sup>14</sup>) W. PALZ and W. RUPPER: *Phys. Status Solidi*, **15**, 665 (1966).

(<sup>15</sup>) S. MORA and N. ROMEO: *Phys. Status Solidi*, **15**, 599 (1976).

(<sup>16</sup>) D. REDFIELD: *Proceedings of the XIV IEE Photovoltaic Special Conference* (1980).



different spectral properties confirms that the measurements can be considered almost independent of some parameters which generally are hardly valuable such as the surface recombination velocity.

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The authors are very grateful to Prof. H. LOZYKOWSKI of the Physics Institute of the Nicholas Copernicus University of Torun for having furnished the CdS crystals and to Prof. C. PAORICI of the Laboratory MASPEC-CNR of Parma for having furnished the CdSe crystals.

#### ● RIASSUNTO

È stata misurata la lunghezza di diffusione dei portatori minoritari su monocristalli di CdS e CdSe utilizzando il metodo del fotovoltaggio superficiale (SPV). Illuminando i campioni attraverso barriere Schottky semitrasparenti è stata rilevata una relazione tra l'intensità di luce incidente e la lunghezza di assorbimento per ogni valore del fotovoltaggio. I valori della lunghezza di diffusione sono stati ottenuti mediante estrapolazione ad intensità di luce nulla usando il metodo dei minimi quadrati. L'accordo tra misure eseguite su diodi preparati in modo differente e con differenti risposte spettrali ha confermato una quasi indipendenza della tecnica SPV da alcuni parametri e condizioni sperimentali.

Резюме не получено.