Solid State Phenomena Vols. 51-52 (1996) pp 373-378

doi:10.4028/www.scientific.net/SSP.51-52.373

Electronic Properties of Defect Levels Investigated by Photocurrent Noise in Polycrystalline Cadmium Compounds

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Keywords: Deep Energy Levels, Current Noise Spectroscopy, Cadmium Compounds

Abstract. Current noise spectroscopy has been widely used to study the electronic structure of surface states and shallow impurity levels of semiconductors. In the present paper an extension of this technique to the study of deep energy levels and of the forbidden energy gap of photoconductors is discussed on the basis of a theory of photoconductance noise developed in previous papers. Results concerning the photoionization cross section and the energy gap of three photoconducting devices, having different spectral characteristics, are presented and compared with the results obtained with other techniques. From this comparison it can be inferred that noise spectroscopy may be a useful complement for the study of the structure of photoconductor forbidden band gap.

Introduction

The use of noise spectroscopy to study the energy distribution of trapping levels related to donor or acceptor centers in semiconductors has been widely employed in the past years [1]. The quantities which are mostly affected by the density and the capture cross-section of the traps are the intensity and the cut-off frequency of the g-r (generation-recombination) noise. Surface trapping states, on the other side, influence the other important component of the current noise in semiconductors, the so called 1/f noise, which is dominating the noise power spectrum at low frequencies.

Noise spectroscopy is currently used to study rather shallow trapping centers in thermal equilibrium condition, where transitions occur by thermal excitation of the centers. Deeper lying centers, both in semiconductors and in insulating photoconductors, are generally investigated by optical or photoelectronic methods [2,3].

In the present paper we shall show that photoconductance noise can be used to study the distribution of deep lying photosensitive centers as well as to perform accurate measurements of the forbidden energy gap in the operative conditions of the device. Spectral response and constant photocurrent measurements have also been compared with the photocurrent noise results.

Photoconduction noise

In order to understand the physical background on which the photocurrent noise spectroscopy is based, a brief account of the photoconduction theory developed in preceding papers [4-6] must be given.

According to this theory, the photoconduction process is controlled by a photosensitive potential barrier due to the band bending in correspondence of the ohmic metal contacts. This barrier is lowered by the positive trapped charge created by the photoionized centers (deep donor centers or trapped holes, depending on the light wavelength in the case of CdS and CdSe), thus allowing electron injection from the electrodes into the conduction band of the photoconducting material. Two main noise components can be envisaged in the photocurrent. One of them is related to the transport process in the photoconducting material and is generated by thermally activated trapping-detrapping events in shallow centers or surface states as it happens in semiconductors (g-r and 1/f noise). It has been referred to as the *intrinsic noise component*. The second component, which will be referred to as *photoinduced*, is typical of the photoconductors and is related to the fluctuation of the height of the potential barrier

due to the spontaneous fluctuations of the number of the photoionized centers. Such component, that in suitable physical conditions dominates the photocurrent noise power spectrum in the low frequency range, gives information on the deep lying centers and on the forbidden energy gap of the photoconducting material. From the general expression of photoconductance noise power spectrum worked out in [4], the following expression of the photoinduced noise spectral component is obtained:

$$\Phi_G^{ph}(\omega) \cong \frac{1}{\pi} \cdot (\Delta g)^2 \cdot n_{fa} \cdot \Sigma_j \frac{\eta_\lambda^{(j)} \tau_d^{(j)2}}{1+\omega^2 \tau_d^{(j)2}} \cdot \tag{1}$$

where n_{fa} is the flux of absorbed photons, Δg is the derivative of the photoconductance with respect to the number of photoionized centers n_d, $\eta_\lambda^{(j)}$ is the photoionization efficiency for a j center, and $\tau_d^{(j)}$ the lifetime of a ionized j center. If the condition:

$$\omega^2 \tau_d^{(j)2} \gg 1 \tag{2}$$

holds, we can write:

$$\Phi_G^{ph}(\omega) = \frac{1}{\pi} \cdot \frac{(\Delta g)^2}{\omega^2} \cdot n_{fa} \cdot \eta_\lambda , \tag{3}$$

where:

$$\eta_\lambda = \Sigma_j \eta_\lambda^{(j)} . \tag{4}$$

Since:

$$n_{fa} \cdot \eta_\lambda = \frac{n_d}{\tau_d}, \tag{5}$$

where the quantity τ_d represents the weighted average of the lifetimes $\tau_d^{(j)}$ with weights $b^{(j)}$:

$$\tau_d = <\tau_d^{(j)}> = \Sigma_j b^{(j)} \tau_d^{(j)} \qquad [\Sigma_j b^{(j)} = 1] \tag{6}$$

one gets:

$$\Phi_G^{ph}(\omega) = \frac{1}{\pi} \cdot \frac{(\Delta g)^2}{\omega^2} \cdot \frac{n_d}{\tau_d} \quad . \tag{7}$$

According to the theory, if the photoconductance G is kept constant by adjusting the light intensity when λ is varied, the quantities Δg and n_d appearing in Eq.(7) remain constant and thus Φ_G^{ph} will depend only on τ_d. The rapid variation that τ_d undergoes in correspondence of λ_{gap} allows the determination of the energy gap of the photoconducting material, as the results reported in the following show.

From the Eq. (3), the quantum efficiency η_λ and photoionization cross-section σ_{ph} can also be obtained:

$$\eta_\lambda = \frac{\Phi_G^{ph}(\omega_o)\cdot\omega_o^2\cdot\pi}{(\Delta g)^2\cdot n_{fa}}\,, \tag{8}$$

$$\sigma_{ph} = \eta_\lambda \sigma_o\,, \tag{9}$$

where σ_o is the optical cross-section, proportional to the absorption coefficient α [7].

If $\alpha d \ll 1$, where d is the thickness of the photoconducting film, σ_{ph} becomes proportional to the internal quantum efficiency η_λ^{int} given by:

$$\eta_\lambda^{int} = \eta_\lambda \cdot a = \frac{\Phi_G^{ph}(\omega_o)\cdot\omega_o^2\cdot\pi}{(\Delta g)^2\cdot n_f}\,, \tag{10}$$

where a and n_f are respectively the absorptance and the flux of not reflected photons impinging on the material. In this condition, the photoionization cross-section can thus be obtained even if optical measurements to determine α cannot be performed.

Experimental results and discussion

The theory has been applied to the determination of the energy gap and of the photoionization cross-section of different photoconducting devices based on polycrystalline CdS_xSe_{1-x} alloys from the Hamamatsu Photonics. Noise measurements were performed with monocromatic light, using the technique described in detail in previous papers [5]. Light wavelength resolution was about 3nm.

Results concerning the measurement of the energy gap by means of the noise technique are reported in Figs. 1-3. The rapid variation of the power spectrum density in correspondence to λ_{gap} is well evidenced and allows an accurate determination of the energy gap in the three devices considered. Its value is reported in the figure captions. Since the samples are commercial, the ratio of the selenium to sulphur atoms is unknown. However, in order to compare the photocurrent noise data with those obtained by means of a more standard photoelectronic technique, the spectral response curves are also reported in each figure.

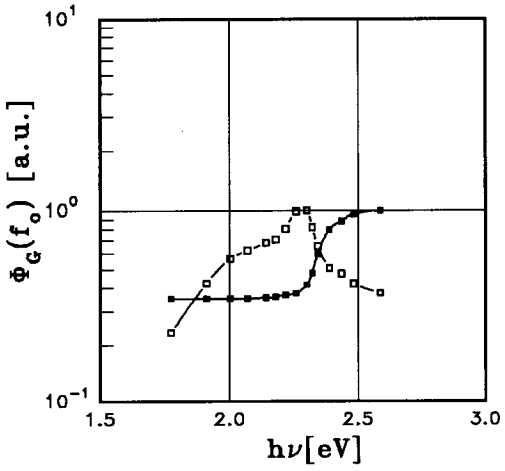

Fig.1 Spectral densities of the conductance fluctuation noise $\Phi_G(f_o)$ as a function of the photon energy of the incident light (filled squares). The noise power spectra were taken at the same value of the electrical conductance $G = 5\cdot 10^{-6} S$ and correspond to a frequency $f_o = 400 Hz$. The value of f_o satisfies the condition (2). The average lifetime τ_d is in fact greater than a few milliseconds for these materials, as it has been proved by photocurrent relaxation measurements.
Hollow squares represent the spectral response (average photoconductance value at constant photon flux). Measurements refer to a P201B CdS_xSe_{1-x} photocell. Extimated value of E_{gap} is $2.35 \pm 0.05 eV$

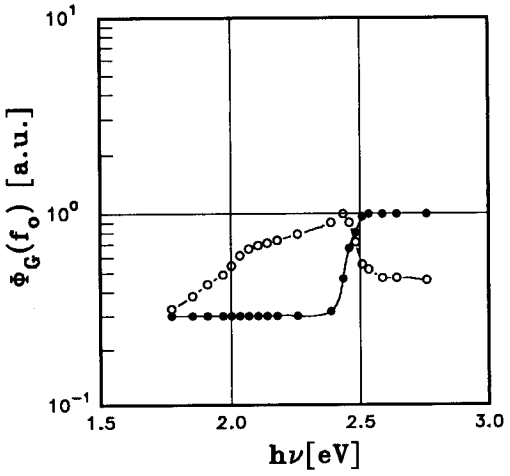

Fig.2 Same as in Fig.1, except that the sample is a P201D CdS_xSe_{1-x} photocell.
Extimated value of E_{gap} is $2.45 \pm 0.05eV$

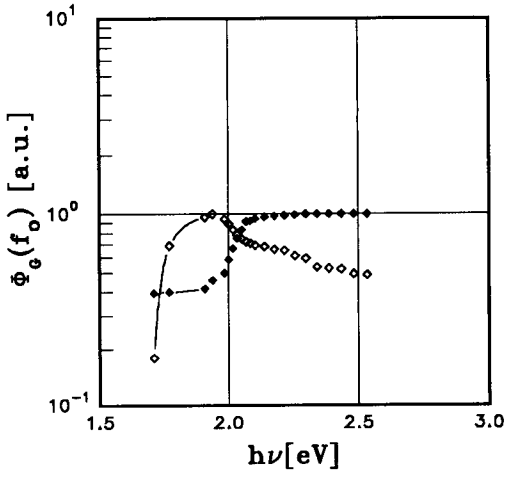

Fig.3 Same as in Fig.1, except that the sample is a P368 Hamamatsu CdS_xSe_{1-x} photocell.
Extimated value of E_{gap} is $2.05 \pm 0.05eV$

In the same figures, the curves representing the photoconductance as a function of the photon energy at constant number of photons are also reported. From these curves the determination of the energy gap of the photoconducting material is rather uncertain, because the photoconductance depends on two parameters (the photoionization efficiency η_λ and the average lifetime of the photoionized centers τ_d) whose variation tends to compensate each other when λ crosses λ_{gap}. On the contrary, as Eq.(7) shows, the photoinduced noise component depends only on τ_d when G is kept constant, and its abrupt variation in correspondence of λ_{gap} allows a neat determination of this last quantity.

Figs.4 and 5 show respectively the behaviour of the inverse of the photon flux n_f at constant G and the internal quantum efficiency η_λ^{int}, obtained from Eqs.(10).

It should be noticed that the curves representing the inverse of n_f vs $h\nu$ at constant G, are often considered to represent the spectral distribution of the photoionization cross section, under the assumption that the average lifetime of the ionized pairs does not change when λ is changed, according to the constant photocurrent technique [8]. In the present case this assumption is not satisfied, particularly close to the energy gap. This explains the difference between the results of the two figures. This limitation could be overcome by performing the constant photocurrent measurements with modulated light. Nevertheless, the use of the photocurrent noise spectroscopy may be preferable, since it is easier to perform and operates closer to the equilibrium condition of the device.

Broken curves in Fig.5 represent the photoionization cross-section obtained following the Lucovsky model [9]. In that paper, the photoionization cross-sections concerning the transitions from discrete impurity levels to a parabolic band are obtained with the assumption of a delta-function potential for the impurity. Such expression contains the ionization energy E_d of the impurity and vanishes when the photon energy is equal to E_d. Thus by keeping the treshold energy E_d as a fitting parameter, deep levels lying respectively at 1.45, 1.6 and 1.7 eV below the bottom of the conduction band are obtained for the three specimens.

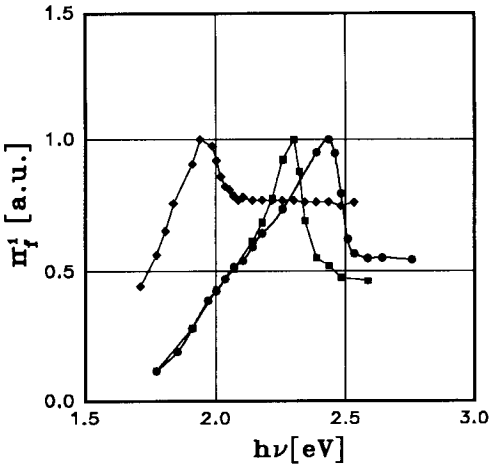

Fig.4 Inverse of the photon flux n_f as a function of the photon energy at constant photoconductance value (respectively for the samples P201D (circles), P201B (squares) and P368 (diamonds)). These data have been introduced in the Eqs.(10) to obtain the average quantum efficiency η_λ and the relative photoionization cross-section σ_{ph}.
According to the constant photocurrent technique, this curves should be approximately proportional to σ_{ph}. The fact that τ_d for these materials is not a constant when λ is changed, causes a certain error in the evaluation of the photoionization cross-section.

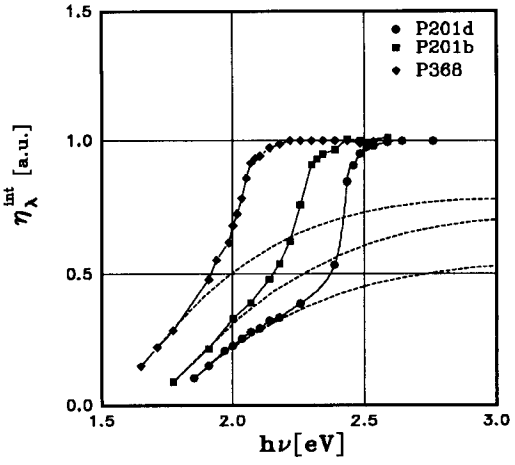

Fig.5 Average photoionization internal efficiency η_λ versus photon energy in the region close to the valence band-edge for the samples P201D (circles), P201B (squares) and P368 (diamonds) obtained from noise measurements using Eq.(10).
Broken lines correspond to the photoionization cross-section obtained according to the Lucovsky model [9].

Summary

The results presented in this paper show that the photocurrent noise spectroscopy can be conveniently used to get information on the band structure of the photoconducting materials. In particular it allows very easily to measure the energy gap and the quantum efficiency η_λ of the photoconducting material, directly on a device in its operative conditions.

Noise spectroscopy has been extensively used to get information on shallow impurity states in semiconductors. This paper shows that it can be conveniently extended to the study of the deep lying centers in photoconductors.

Acknowledgement

We would like to thank Ing. Maerna of the Hamamatsu Photonics Italia for kindly supplying the samples.

References

[1] B.K.Jones, IEEE Trans. **ED-41**, 11, (1994)

[2] M.L.Cohen and J.R.Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors* (Springer-Verlag, Berlin Heidelberg, 1988).

[3] *Handbook on Semiconductors, Vol.1-2, W.Paul and M.Balkansky Eds.*, (North Holland Publ. Comp., Amsterdam-New York, 1982)

[4] A.Carbone and P.Mazzetti, Phys.Rev. **B49**, n.11, 7592, (1994)

[5] A.Carbone and P.Mazzetti, Phys.Rev. **B49**, n.11, 7603, (1994)

[6] A.Carbone and P.Mazzetti, Phys.Rev. **B51**, n.19, 13261, (1995)

[7] R.H. Bube, *Photoelectronic Properties of Semiconductors*, (Cambridge University Press, 1992)

[8] H.G.Grimmeiss and L.A. Ledebo, J. Appl. Phys., **46**, 2155 (1975)

[9] G. Lucovsky, Solid State Commu., **3**, 299, (1965)

Polycrystalline Semiconductors IV
doi:10.4028/www.scientific.net/SSP.51-52

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