

A Study of Electron Traps in Vapour-Phase Epitaxial GaAs

A. Mircea and A. Mitonneau

Laboratoires d'Electronique et de Physique appliquée 3, Avenue Descartes, F-94450 Limeil-Brévannes, France

Received 2 May 1975 / Accepted 2 June 1975

Abstract. The occurrence and physical properties of electron traps in device-quality VPE *n*-GaAs are studied using transient capacitance and DLTS (deep level transient spectroscopy). Four traps labeled A, B, C, and F are seen. Trap A is identified to be the same as the often reported one, commonly attributed to oxygen in substrate material; this trap is also dominant in the VPE layers. The other traps are (to our knowledge) reported here for the first time. No correlation appears to exist between the concentrations of the various traps. The emission rate vs. temperature dependence, a characteristic physical property, is obtained for each of these traps.

Index Headings: Gallium arsenide – Vapour epitaxy – Electron traps – Transient capacitance – Deep level transient spectroscopy

In recent years the art of GaAs epitaxial growth has made significant advances, so that it is possible nowadays to obtain sophisticated multi-layer structures with a good control of dopant concentrations and layer widths [1]. Several new (or less new) applications may be considered, however, for bipolar devices at least, the existence in this material of deep discrete states in considerable concentrations is an obvious limitation [2], so that an increasing effort is being spent in several laboratories in order to assess the deep level content with respect to concentration, electronic properties and physico-chemical origin.

Another incentive for the study of deep levels in III—V compounds comes from the field of electro-luminescent devices. Both the initial performance and the reliability of these are strongly influenced by deep states acting as excess carrier lifetime killers [3].

Finally, for the solid-state physicist, the study of deep states in III–V semiconductors is a challenging subject. It has already been shown that – with respect to the nature of electronic transitions – these states present

peculiar properties such as multiphonon emission [4] and localized transitions [5]. Moreover very little is known about the physico-chemical origin of these levels, i.e. whether they are due to impurities or crystalline defects or combinations of both.

In order to answer all these questions the converging activity of many people is necessary. In the following report we try to contribute to this effort through new experimental observations on the occurence and properties of deep electron traps in device-quality VPE gallium arsenide.

A powerful means for detecting and characterizing the deep traps consists of monitoring the depleted layer capacitance of a Schottky barrier or p-n junction made on the semiconductor under study. Many possible variations of this basic experiment, involving electrical or optical excitation of the electronic transitions, have already been proposed or may be imagined. The transient capacitance experiment proposed by Williams [6] and subsequently refined [7–9, 13–14] is a very useful method of investigation. The recent contribution, by Lang, of DLTS (Deep Level Transient Spectroscopy) [10,

11, 17], which is a dynamic, time-differential variant of transient capacitance, significantly enlarged its capabilities by making it possible to obtain a large amount of information in a short time. In our work we used the transient capacitance method both in its "classical" and DLTS form. The results were also compared with those of photocapacitance experiments made on the same samples.

Theory

The steady-state fractional occupancy of a discrete energy level is [12]

$$f_{tss} = (c_n n_{ss} + e_n)/(c_n n_{ss} + e_n + c_n p_{ss} + e_n)$$
 (1)

where $e_n(e_p)$ is the free electron (hole) emission rate, $c_n(c_p)$ represents the free electron (hole) capture coefficient, $n_{ss}(p_{ss})$ denotes the steady-state free electron (hole) density.

In the depleted layer of a Schottky barrier or p-n junction, n_{ss} and p_{ss} are extremely small so that (1) may be reduced to

$$f_{tss} \simeq e_n/(e_n + e_n)$$
 (carrier depletion). (2)

Let us specifically consider an "electron trap" for which, by definition, $e_p \ll e_n$ in the temperature range considered. Then, $f_{tss} \ll 1$ so that the traps are empty in steady-state conditions.

The electron trap energy levels are more likely to be found in the upper half of the forbidden gap. However, this restriction is not absolute. Particular caution must be given before using the simplified expression (2) for traps near or below the mid-gap level.

In the transient capacitance experiment the traps are (partially or completely) filled at $t \le 0$ by suitable electrical or optical excitation, then at $t \ge 0$ the barrier (or p-n junction) is reverse biased so that, in the depleted region, the traps empty out exponentially. The time constant for trap emptying is

$$\tau_e = (e_n + e_p)^{-1} \tag{3}$$

or $\tau_e \simeq e_n^{-1}$ for electron traps. We recall that [12]

$$e_n = (4\sqrt{6}\pi^{3/2}h^{-3}m_n^*k^2)\sigma_n T^2 \exp[(E_t - E_c)/kT],$$
 (4)

where σ_n is the electron capture cross-section, $(E_t - E_c)$ represents the trap energy level referred to the conduction band minimum, m_n^* denotes the free electron mass; a similar expression holds for e_p . In GaAs, with $m_n^* = 0.07 m_0$ the parenthesis preceding σ_n in (4) amounts to $2.28 \ 10^{20} \ \text{cm}^2 \ \text{s}^{-1} \ (\text{K})^{-2}$.

The above statement of exponential emptying assumes that no retrapping of the freed carriers occurs. Again this assumption should be carefully checked in particular situations.

The transient variation of space-charge due to emptying traps is observed experimentally by monitoring the depleted-layer capacitance. Two possibilities appear:

(i) maintain a constant reverse bias and record the variation of capacitance (space-charge layer width), or (ii) by using an external feedback loop, maintain a constant capacitance and record the variation of reverse bias.

The second variant has distinct advantages with respect to the subsequent analysis of data [13, 14]. In our present work we used the first variant since it is somewhat easier to implement experimentally. In this case, the capacitance transient is not exponential, even if the trap emptying process is so, because the extension of the region where this process occurs varies in time also. A detailed treatment of this problem was given in [15].

The result can be expressed in a simple form in the particular cases where (i) the trap density N_t and the permanently ionized level density N_s are spatially uniform, and (ii) the initial state (at $t \le 0$) corresponds to complete filling of the traps, i.e., the barrier (or junction) is forward-biased to flat-band.

With these restrictions in mind, the following result may be derived from [15].

$$N_{te}(t)/N_s = [N_{te}(\infty)/N_s] [1 - \exp(-e_n t)]$$

= $[C^2(t) - C^2(0)]/[C(0) - \gamma C(t)]^2$ (5)

with

$$\gamma = \left[(E_F - E_t) / q(V_a + V_d) \right]^{1/2}, \tag{6}$$

where N_{te} is the density of empty traps; N_s designates the density of permanently ionized, net positive, fixed space-charge; C(t) is the time-varying depletion-layer capacitance; E_F denotes the Fermi energy level in the bulk (neutral) semiconductor; V_a is the applied reverse bias and V_d the built-in diffusion potential.

It is seen that a relatively complex algebraic manipulation of the measured C(t) data is necessary in order to have access to a simple exponential variation, from which the emission rate e_n and the relative trap concentration $N_t/N_s \simeq N_{te}(\infty)/N_s$ can be obtained. Moreover, γ depends on the trap energy level, so that formula (5) can only be applied if this property is (approximately at least) known beforehand.

Fortunately, for good quality material in which $N_t \leq N_s$ formula (5) simplifies to

$$N_{te}(t)/N_s = [N_{te}(\infty)/N_s] [1 - \exp(-e_n t)]$$

$$= 2\Delta C(t) [(1 - \gamma)^2 C(t)]^{-1}$$
(7)

so that the capacitance variation itself becomes a simple exponential. For most of the data to be reported below, approximation (7) was a very good one. In such cases the treatment of more complicated situations such as, for instance, non-uniform $N_t(x)$ and $N_s(x)$ or simultaneous emptying of several different traps is greatly facilitated.

Experimental Set-Up and Procedure

The implementation of the transient capacitance (and DLTS) was achieved using commercially available equipment which was already in use for doping profile evaluation from C(V) measurements. A flexible system was built around a H & P 9810A calculator which controls the excitation and the temperature variation, collects the data, operates the necessary calculations on them and displays the final result in graphical and/or numerical form. The forward-bias excitation is achieved through a 11202A interface; the capacitance measurement is transferred through a digital voltmeter from a Boonton 71E capacitance meter to the calculator, and another digital voltmeter serves the same purpose for temperature readings.

With such a system the different variations of the basic experiment are easily and quickly interchanged by suitable software manipulations. Another advantage is the immediate availability of the completely processed result.

Two particular points deserve special mention. Firstly, the relatively narrow bandwidth of the capacitance meter (about 100 Hz) sets a lower limit to the time scale which can be explored. The fastest measurable emission rate is about 50/s; most of the data were taken for emission rates of 8/s or less (down to 0.04/s). Second, considerable care was devoted to the attainment of good accuracy of temperature measurements, especially in dynamic (variable temperature, as necessary for DLTS) conditions. To this end, we used as temperature transducer a carefully burned-in and calibrated GaAs p-n junction which is mounted sideby-side with the sample in closely similar thermal conditions, so that, even if the transducer is electrically isolated from the sample, the temperature variation is identical for both. This was verified by replacing

the sample with a second transducer; at the fastest temperature variations used (about 10 deg/min) the observed differences were well within the calibration uncertainty.

For a detailed description of the DLTS technique we refer to the original papers by Lang [10, 11, 17]. In order to achieve a given emission rate "window" we used the simple time-differential measurement described in these papers, i.e., we measure the capacitance at two fixed times t_1 , t_2 following the end of the excitation pulse and we compute the expression

$$M(t_1, t_2) = 2[C(t_2) - C(t_1)]/C(t_1) \cdot K(t_2/t_1)$$
(8)

with

$$K(x) \equiv \lceil x/(x-1) \rceil \exp\lceil \ln x/(x-1) \rceil \tag{9}$$

and $x = t_2/t_1$.

The factor $[K(x)]^{-1}$ is the maximum value of the difference $[\exp(-et_1) - \exp(-et_2)]$, obtained for $e = e_0$, the center value of the emission rate window:

$$e_0 = [\ln(t_2/t_1)]/(t_2 - t_1). \tag{10}$$

Thus, when approximation (7) is valid, the observed maximum of $M(t_1, t_2)$ as a function of temperature equals [but for the factor $(1-\gamma)^2$] the relative trap concentration $N_{te}(\infty)/N_s$. The smallest measurable N_t/N_s in our set-up is about 1/5000, limited by system noise. Data averaging over several cycles, done by the calculator, is used to get this result. As pointed out by Miller [16], cross-correlation with an exponential waveform would certainly improve the signal-to-noise ratio. The data reported below were obtained with Schottky-barrier samples, therefore only majority-carrier (electron) traps could be detected [7].

Results

a) Inventory and Concentration Range of Observed Electron Traps

Many DLTS spectra were taken on various samples, mostly VPE, but also substrate material and liquid-phase epitaxy for comparison. A few examples are presented below, selected so as to summarize qualitatively all our observations.

The richest spectra were obtained on melt grown material, as illustrated in Fig. 1a, where five peaks labeled A-B-C-D-E can be clearly seen, while a sixth one (A') is suggested by a shoulder on the curve. Peaks D and E are only partially resolved.

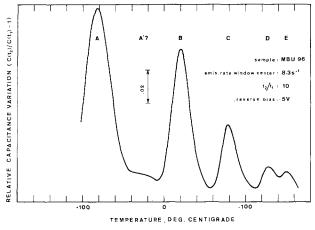


Fig. 1a. DLTS spectrum of boat-grown GaAs, $n \simeq 10^{16}$ cm⁻³ at 300 K

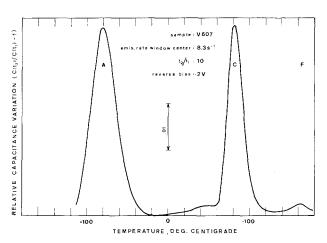


Fig. 1d. DLTS spectrum of VPE GaAs, $n \simeq 10^{14}$ cm⁻³ at 300 K

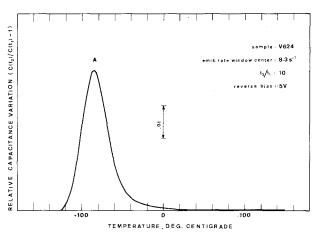


Fig. 1b. DLTS spectrum of VPE GaAs, $n \simeq 2.10^{14}$ cm⁻³

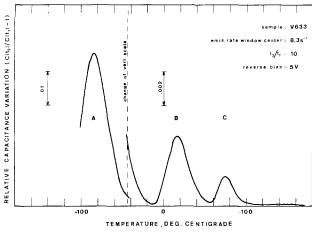


Fig. 1e. DLTS spectrum of VPE GaAs, $n \approx 8.10^{14}$ cm⁻³

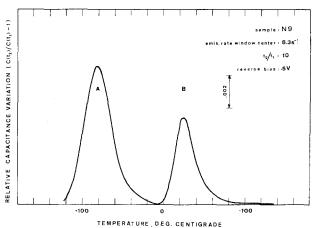


Fig. 1c. DLTS spectrum of VPE GaAs, $n \simeq 3.10^{14}$ cm⁻³

At the other extreme of spectrum complexity, no electron traps at all could be detected in LPE material $(10^{15} \text{ cm}^{-3} \text{ free electron density})$. This is in agreement with other studies [11].

The situation encountered with VPE (AsCl₃ process on 3-degree misoriented 100 planes) is illustrated by Figs. 1b to e, all of which refer to Schottky barriers (Au or Pt) on wafers with $n=10^{14}\dots 10^{16}$ cm⁻³ which were not subjected to any other treatment after epitaxy.

The spectrum in Fig. 1b shows only one peak, identified by comparison with Fig. 1a to be the same trap "A" as in the substrate material. In Fig. 1c, peaks "A" and "B" are observed. Likewise, in Fig. 1d, only peaks "A" and "C", plus a new, weak peak labeled "F" can

Table 1. Range of electron trap densities observed in VPE n-GaAs

Trap	Rate of occurence	Range of concentrations [cm ⁻³]	Remarks
A	occurs systematically	10 ¹² to several 10 ¹⁴	
В	frequent	up to several 10 ¹³	
C	frequent	up to several 10 ¹³	
D	not observed yet		
E	not observed yet		may be the same as trap F
F	only in a few samples	up to several 1012	•

be seen. Finally, in Fig. 1e the ever present peak "A" is accompanied by both peaks "B" and "C".

These examples exhaust the list of the peaks we have seen as yet in a large number of VPE wafers coming from several reactors. They also illustrate the fact that no definite correlation exists between the occurence of the various peaks, except for the predominance of peak "A". Moreover, with one possible exception (peak "F") the same peaks are identified in both vapour-epi and melt-grown GaAs.

The quantitative assessment of trap densities is readily done with formulas (5) to (7) above, provided that (i) the factor γ is approximately evaluated and (ii) one makes sure that the traps and the shallow levels are uniformly distributed. The first point is discussed in the next paragraph; the second one was checked on some of the samples by taking spectra with several values of reverse bias and applying a suitable mathematical treatment. The results are summarized in Table 1.

b) Physical Properties of the Traps

Basically, the information obtained from the transient capacitance experiment consists of the dependence $e_n(T)$ – emission rate versus temperature – which is by itself a physical property of the trap. This information is presented in Fig. 2 for all the peaks observed by us. On the same figure, data taken from previous publications are also plotted for comparison.

This figure clearly shows that most of the previous observations refer to trap "A" and also that a good agreement exists between the various sources concerning this trap, even if the subsequent analysis (in terms of energy levels and capture cross-sections) of the experimental data led sometimes to quite different interpretations. We recall that several of these studies refer to melt grown, oxygen doped material; for this

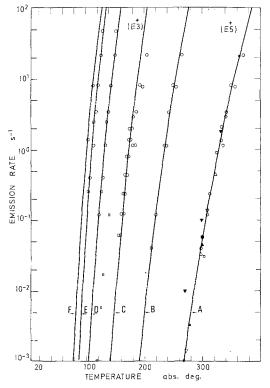


Fig. 2. Electron emission rate vs absolute temperature for the six electrons traps observed in VPE and substrate material. 0 this work; \blacktriangle : [6]; \bigtriangleup : [8]; +: [11]; ∇ : [13]; \blacksquare : [15]; \bullet : [18]; \Box : [19]; \blacktriangledown : [20]. The full curves are calculated according to formula (12) with ΔE and σ_0 as given in Table 2

reason, it is commonly assumed that trap A is connected in some way to the presence of oxygen ¹.

As regards the other peaks B to F, very few – if any – information appears to have been reported. We only can mention the observation of a trap (labeled " T_3 " in [19]) whose properties approach those of our peak D, while the difference (about 15 to 17 degrees at a given value of e_n) in the respective $e_n(T)$ curves is still unreasonably large. From [11] we get the two points labeled (E3) and (E5) on our Fig. 2; these refer to traps voluntarily created in (originally trap-free) LPE material by 1 MeV electron irradiation. Obviously, (E5) is not the same but looks quite like trap A; the resemblance is even stronger between (E3) and trap C, and it may well be that E3 is the same as C but more experimental evidence is needed to as certain this point.

¹ Preliminary results of heat treatment experiments on VPE layers suggest in fact that a cristalline defect (Ga vacancy?) is basically involved in the creation of this trap. We intend to report the conclusions of this work in the near future.

Table 2. Activation energies and apparent capture cross-sections of the observed electron traps in *n*-GaAs

Trap	Activation energy ΔE , eV	Apparent capture cross-section σ_0 , cm ²	Temperature range [K]
A	0.825 (+0.040, -0.010)	(0.8–1.7) 10 ⁻¹³	265-370
В	0.575 ± 0.025	$(0.8-1.7)\ 10^{-13}$	210-265
C	0.420 ± 0.015	$(0.5-2.)$ 10^{-13}	155-195
D	0.275 ± 0.010	$7.7 10^{-15}$	120-150
Ε	0.225 ± 0.015	$6.8 10^{-15}$	105-130
F	0.180	3.10^{-16}	100-115

At this point of the discussion it may be appropriate to mention that the $e_n(T)$ curves measured for the same peak on different samples were not always exactly the same, with differences well above the experimental error. The observed trend is that essentially the same slope (activation energy), is obtained on all samples, however the curves are slightly translated vertically from one another so that, for a given value of the emission rate window center, variations of the peak temperature within a range of 8–10 degrees are definitely observed. This point was repeatedly checked; even with the different samples mounted on the same copper stud (to make sure that the temperature is the same), the differences subsisted.

Since the relative trap concentrations $N_{\rm I}/N_{\rm s}$ in these samples are small, time-constant corrections such as discussed in [15] are negligible. Also, the influence of the electric field on emission rates can be ruled out since the position of the peak was essentially independent of reverse bias. Thus we must conclude that some variation of the physical properties of the traps really exists, and it may be of scientific interest to look at this point in more detail.

The emission rate data can, of course, be analyzed in terms of an activation energy ΔE and an apparent capture cross-section σ_0 , as suggested by expression (4) above, however one should not overlook the fact that the real capture cross-section $\sigma_n(T)$ can be a strongly increasing function of temperature [4], so that if one writes

$$\sigma_{n}(T) = \sigma_{0} \exp(-W_{\sigma}/kT) \tag{11}$$

then from (4) one gets for GaAs

$$e_n(T) = 2.28 \cdot 10^{20} T^2 \sigma_0 \exp(-\Delta E/kT)$$
 (12)

with

$$\Delta E = E_c - E_t + W_\sigma \,. \tag{13}$$

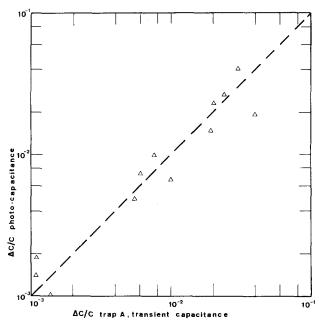


Fig. 3. Correlation between transient capacitance results for trap A and simplified photo-capacitance experiment (see text) results on samples coming from the same wafer. Each point corresponds to a different wafer

The estimates we get from our experimental data for ΔE and σ_0 are summarized in Table 2; the dashed lines in Fig. 2 correspond to these estimates.

The activation energy for trap A is in agreement with [4], since according to Fig. 1 (trap O–GaAs) of this reference $(E_c-E_t)=0.75$ eV and $W_\sigma\simeq 0.08$ eV in the temperature range 150 to 300 K. However, the capture cross-sections do not agree since $\sigma_0\simeq 7.5\ 10^{-15}\ {\rm cm}^2$ from the same figure. At 300 K, $\sigma_n\simeq 4.10^{-16}\ {\rm cm}^2$ from [4]; from our σ_0 and $W_\sigma=0.08$ eV we get $\sigma_n\simeq (4...8)\ 10^{-15}\ {\rm cm}^2$, in agreement with Williams [6] who estimated it at 1.3 to 9.3 $10^{-15}\ {\rm cm}^2$.

For traps B to F, independent measurements of the real capture cross-sections as a function of temperature are needed.

c) Comparison with Photo-Capacitance Experiments

An independent method for observing deep levels – photo-capacitance [21] – was already in current use in our laboratory so that it has been possible to compare data taken on the same samples. The photo-capacitance experiment is a simplified one: samples are cooled in the dark under zero bias from room temperature to 77 K, then a fixed reverse bias is applied and the capacitance $C_{\rm dark}$ is measured. Then,

light from a GaAs electroluminescent diode operating at room temperature is thrown on the sample via a light pipe. The new steady-state capacitance $C_{\rm light}$ is measured and the relative variation $2(C_{light} - C_{dark})$ $C_{\rm dark}$ is taken as a measure of the trap content N_t/N_s . The detailed interpretation of this simple, routine experiment is not easy for several reasons, one of which being that a priori several traps may be involved. However, when we plot, as in Fig. 3, on a log-log scale the rough $\Delta C/C$ results of photo-capacitance versus those obtained for trap A in the transient capacitance experiment, it turns out that the points fall near enough to a straight line of slope unity. It is thus confirmed that (i) trap A is predominant in all these (VPE) samples, and (ii) trap A is effectively emptied by the 0.85 μ m light of the electroluminescent diode.

Conclusion

Four different electron traps were observed in *n*-type vapour epitaxial GaAs layers of device quality. The observed concentrations of these traps fall in a wide range and no definite correlation appears to exist between them, except for the fact that the one labeled "A" in this work appears to predominate in all samples. This same trap is recognized to be the often-reported one usually attributed to oxygen, and it is shown that its electronic properties are reasonably well understood.

The other three traps labeled B, C and F are probably reported here for the first time; traps B and C were seen both in epi – and boat – grown material; for this last type of material two more traps labeled D and E were also observed.

We intend to complete this study with determinations of the real capture cross-sections of the newly observed. traps. Clearly, more effort is needed in order to throw some light over the mistery of the physico-chemical origin of the traps, and to bring them into control.

Acknowledgment. We are grateful to L. Hollan for most of the VPE samples; E. Fabre, T. Ikoma, C. H. Henry, D. Lang for exchange of informations; D. Bois, A. Humbert, G. Laurence for the photocapacitance data; and R. Veilex for moral support.

References

- Proc. 5th Intern. Symp. GaAs, Deauville 1974 (Inst. of Physics, London) to be published
- 2. A.M.Mohsen, M.F.Tompsett: IEEE Trans. Electron Dev. ED-21, 701 (1974)
- 3. T. Ikoma, T. Okumura: ESSDERC 1974 (unpublished)
- C.H.Henry, D.V.Lang: Proc. 12th Intern. Conf. Physics of Semiconductors, Stuttgart 1974, ed. by M. Pilkuhn (B. G. Teubner, Stuttgart 1974) (ISBN 3-519-03013-6) 411
- 5. D. Bois, P. Pinard: Phys. Rev. B 9, 4171 (1974)
- 6. R. Williams: J. Appl. Phys. 37, 3411 (1966)
- 7. C.T.Sah, L.Forbes, L.L.Rosier, A.F.Tasch Jr.: Solid-State Electronics 13, 759 (1970)
- 8. G.H.Glover: IEEE Trans. Electron Dev. ED-19, 138 (1972)
- 9. T. Ikoma, B. Jeppsson: Japan. J. Appl. Phys. 12, 1011 (1973)
- 10. D.V. Lang: J. Appl. Phys. 45, 3023 (1974)
- D.V.Lang, L.C.Kimerling: Intern. Conf. Lattice Defects in Semiconductors, Freiburg 1974 (Inst. of Physics, London) to be published
- 12. J.S.Blakemore: Semiconductor statistics (Pergamon Press, Oxford 1962)
- G. Goto, S. Yanagisawa, O. Wada, H. Takanashi: Appl. Phys. Letters 23, 150 (1973)
- 14. J.A. Pals: Solid State Electr. 17, 1139 (1974)
- 15. M. Bleicher, E. Lange: Solid-State Electronics 16, 375 (1973)
- 16. G.L. Miller: Intern. Conf. Lattice Defects in Semiconductors, Freiburg 1974 (Inst. of Physics, London) to be published
- 17. D.V.Lang: J. Appl. Phys. 45, 3014 (1974)
- 18. R.R. Senechal, J. Basinski: J. Appl. Phys. 39, 4581 (1968)
- 19. K. Sakai, T. Ikoma: Appl. Phys. 5, 165 (1974)
- 20. Y. Furukawa, Y. Ishibashi: Japan. J. Appl. Phys. 5, 837 (1966)
- 21. D. Bois, M. Boulou: Phys. Stat. Sol. (a) 22, 67 (1974)