Extended Abstracts of the 19th Conference on Solid State Devices and Materials, Tokyo, 1987, pp. 83-86

B-2-1

Invited

Photo-and Electroluminescence Investigation of Rare Earth Ions in III-V Semiconductors

Helmut Ennen

Fraunhofer-Institut für Angewandte Festkörperphysik

Eckerstrasse 4, D-7800 Freiburg, West-Germany

Sharply structured photoluminescence bands were observed in the III-V semiconductors InP, GaP, and GaAs doped with the rare earth ($4f^n$)-ions Yb, Er, Nd and Pr. These emission bands in the near infrared spectral region are due to internal 4f - 4f transitions of trivalent $4f^n$-ions. Zeeman measurements, optically detected magnetic resonance, electron spin resonance and photoluminescence excitation measurements were performed to determine the structure of the $4f^n$-centers and to separate different rare earth complexes. The characteristic intra 4f-shell transitions could also be excited electrically in 4f-doped pn-diodes and laser diodes giving rise to incoherent and coherent radiation around 1.0 µm and 1.54 µm.

1. Introduction

The investigation of the luminescence properties of rare earth ($4f^n$)-ions in solids is an important branch in solid state physics since several decades. This research has concentrated dominantly on ionic hosts such as oxides and fluorides /1/ and to a much lesser extent on II-VI semiconductors /2/.

The most remarkable feature of these ions is the spectral sharpness of their 4f-emissions even at room temperature, which results from the shielding of the inner lying 4f-shell by the outer filled $5s^2$ and $5p^6$ orbitals. Due to the small interaction of the 4f-orbitals with the crystalline environment rare earth ions exhibit characteristic intra 4f-shell transitions in the visible and in the near infrared spectral region. The high solubility of 4f-ions in insulating hosts is a reason why they were studied extensively as the gain media in externally pumped laser crystals such as Nd^{3+}:YAG /1/ and Er^{3+}:$YAlO_3$/3/.

Since a few years the investigations of the luminescence of 4f-ions in solids concentrated also on the technologically important III-V semiconductors and silicon, also with the aim to achieve novel types of optoelectronic devices. This article reviews briefly the spectroscopic investigations of the trivalent $4f^n$-ions Yb^{3+} ($4f^{13}$), Nd^{3+} ($4f^3$), Pr^{3+} ($4f^2$) and Er^{3+} ($4f^{11}$) in the III-V semiconductors InP, GaP, and GaAs. The feasibility of producing light emitting diodes and laser diodes by different kinds of epitaxial growths processes will also be reviewed.

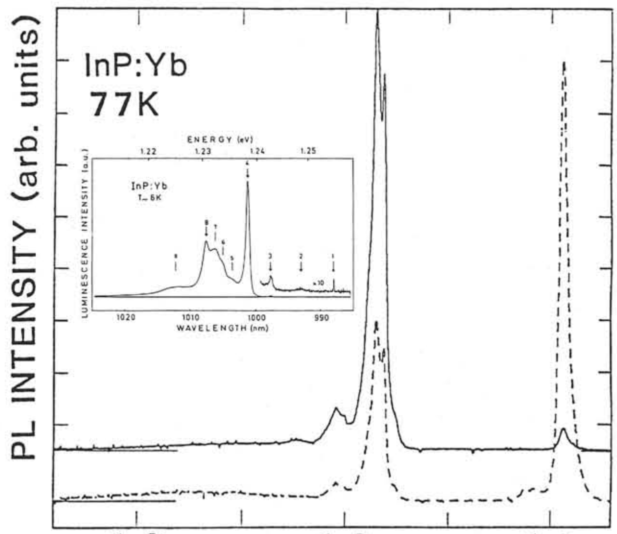

Fig. 1: Luminescence spectrum of InP:Yb grown by MOCVD /15/. The insert shows the high resolution spectrum of Yb^{3+} /17/.

2. Results and Discussion

Ytterbium (Yb) in InP, GaP, and GaAs

The first case of a rare earth ion related emission was observed for Yb-doped InP grown by molten solution /4-6/ and for Yb-doped GaP grown by the same technique /7-9/. This luminescence band was also observed for Yb-implanted InP, GaP, and GaAs samples after proper annealing steps /10-12/. The possibility to grow Yb-doped InP epitaxial layers by liquid phase epitaxy (LPE) and metal organic chemical vapour deposition (MOCVD) was demonstrated by Haydl et al. /13/ and Uwai et al. /14, 15/, respectively; Fig. 1. The observed transition around 1.0 µm in these Yb-doped III-V semiconductors is due to the internal 4f - 4f transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Yb^{3+} ($4f^{13}$). The fine structure in the low temperature photoluminescence spectra results from the crystal field splitting of the spin-orbit levels; see insert of Fig. 1. The excited states of the luminescent level in InP:Yb were determined by photoluminescence excitation spectroscopy /16/. Zeeman measurements /17/ and optically detected magnetic resonance /18/ revealed that the Yb^{3+} spectrum in InP arises entirely from only one type of cubic Yb^{3+}-center, which resides presumably on a substitutional cation site. Besides this dominant cubic (Td) Yb^{3+}-center an Yb^{3+}-center with trigonal symmetry (line No. 1, see insert of Fig. 1) was identified /11/. Electron spin resonance on InP:Yb was observed and revealed a g-factor for the Γ_6 ground state with $g = 3.291 \pm 0.001$ /19-21/, which is somewhat larger than the one determined by Zeeman measurements /17/.

Neodymium (Nd) in GaP and GaAs

Three sets of sharp emission lines were observed for Nd-implanted GaP due to the intra-center transitions $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (900 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1100 nm) and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1400 nm) of Nd^{3+} ($4f^3$) /22/. Similar emission spectra were also recorded in Nd-implanted GaAs /22/. Isothermal and isochronal annealing studies and photoluminescence excitation measurements /23/ revealed that the multiplicity of the observed emission lines arises from different Nd^{3+}-centers with non cubic symmetry /22, 23/. The nature of the defects which destroys the cubic symmetry is not known as yet.

Praseodymium (Pr) in GaP

A rich structured Pr-related emission spectrum could be detected in Pr-doped GaP grown by molten solution. This intra 4f-shell transition of Pr^{3+} ($4f^2$) could only be observed after heat treatment of the sample /8/. If Pr was implanted in GaP and co-implanted with Li different emission spectra were recorded /24/ presumably due to an association of Pr with Li.

Gadolinium (Gd) in InP

No luminescence data exist for Gd^{3+} ($4f^7$) in III-V semiconductors, but electron spin resonance due to Gd^{3+} could be observed in InP /25/ grown by molten solution. The fine structure lines with $g = 1.985 \pm 0.005$ result from a Gd^{3+}-center in the $^8S_{7/2}$ ground state exhibiting cubic symmetry. Furthermore, a Gd^{3+}-center with lower than cubic symmetry was detected.

Erbium (Er) in InP, GaP, and GaAs

A luminescence band around 1.54 µm due to the internal transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ($4f^{11}$) was observed in Er-implanted InP, GaP,

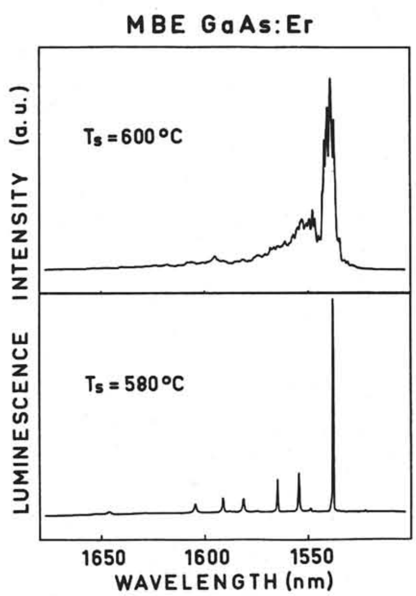

Fig. 2: Effect of substrate temperature T_S on the Er^{3+}-emission at 1.54 µm. Excitation: 514.5 nm, T=6 K /31/.

and GaAs /26-28/. Different annealing conditions result in the creation of several kinds of Er^{3+}-centers in GaAs /28/ presumably due to Er^{3+}-complexes. In Bridgman grown GaAs:Er a luminescence spectrum was recorded with only a few lines which are different from those observed in Er-implanted samples /12/. Er-doping during epitaxial growth like LPE /21,29 / and MBE /30/ results also in quite different emission spectra of Er^{3+} around 1.54 μm.
For MBE-grown GaAs:Er layers the structure of the luminescence spectrum depends on the substrate temperature /31/; see Fig. 2. The linewidth of the main emission line at 1.542 μm (lower part of Fig. 2) is very small and amounts to 0.5 cm^{-1}. Higher resolution spectra taken with a Fourier transform spectrometer (FTIR) reveals a linewidth of 0.04 cm^{-1} /32/ at low temperature. At room temperature the halfwidth is of the order of 10 cm^{-1}. The analysis of the temperature dependent photoluminescence measurements and photoluminescence excitation measurements /31/ on MBE GaAs:Er which exhibits a luminescence spectrum as shown in the lower part of Fig. 2 indicates that this spectrum arises entirely from an Er^{3+}-complex with non cubic symmetry. Zeeman measurements /32/ have shown that the Er^{3+}-center has C_{1h} symmetry. On the other hand Zeeman measurements on LPE-GaAs:Er reveals that this Er^{3+}-center has cubic symmetry /29/.

Electroluminescence

Yb-doped InP layers grown by molten solution /33/ and LPE /13, 34/ were used to prepare light emitting devices. It was shown that the internal 4f - 4f transitions $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Yb^{3+} at 1.0 μm could be excited electrically in these pn-diodes. The variation of the electroluminescence intensity of Yb^{3+} with applied voltage indicates that the space charge recombination current might be responsible for the excitation of the Yb^{3+}-emission /13/. The external quantum efficiency for the Yb^{3+}-emission is of the order of 10^{-3} at 77 K.
Light emitting diodes prepared from MBE-GaAs:Er /35/ and MBE-Si:Er /36/ show emission spectra around 1.54 μm due to the internal 4f - 4f transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ of Er^{3+} ($4f^{11}$).
All the above mentioned 4f-related emissions in III-V semiconductors and silicon were observed at wavelengths which are longer than those of the band edge emission of the host semiconductors. A new type of a 4f-doped laser structure was published by Tsang et al. /37/ and van der Ziel et al. /38/. In this hetero-epitaxial ridge overgrown laser structure the band edge emission wavelength of the quaternary III-V semiconductor was somewhat longer than the Er^{3+} emission wavelengths. These InGaAsP:Er injection lasers where the Er-ions are imbedded in the active layer, exhibit single longitudinal mode operation at 1.5322 μm which can already be observed at 300 K /37/, see Fig. 3. This lasing line shifted at a slow rate of 1 Å/°C with heat sink temperature /37/ which has to be compared to the drastic shift of the emission wavelengths (6.5 Å/°C) of the non Er-doped quaternary semiconductor lasers.

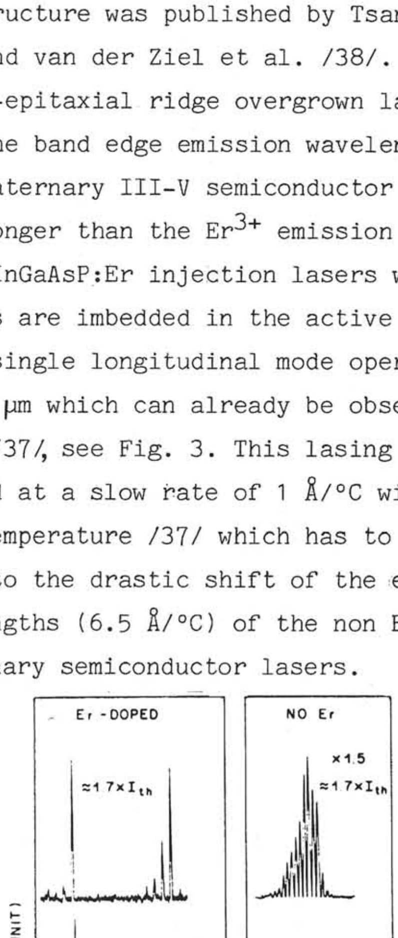

Fig. 3: Lasing spectra of an Er-doped HRO laser and a non Er-doped HRO laser at different current injection levels /37/.

3. Acknowledgement

The author would like to thank J. Schneider for comments on the manuscript and many stimulating discussions. The fruitful cooperation with all the co-authors cited in the reference list will also be greatly acknowledged.

References

/ 1/ A.A. Kaminskii: Laser Crystals (Springer, Berlin, 1981) 322.

/ 2/ M.R. Brown, A.F.J. Cox, W.A. Shand and J.M. Williams: Advances in Quantum Electronics, ed. by D.W. Goodwin (Academic, New York, 1974) Vol. 2, 69.

/ 3/ B. Dischler and H. Ennen: J. Appl. Phys. 60 (1986) 376 and references therein.

/ 4/ L.F. Zakharenkov, V.A. Kasatkin, F.P. Kesamanly, B.E. Samorukov and M.A. Sokolova: Sov. Phys. Semicon. 15, (1981) 946.

/ 5/ L.K. Ermakov, V.A. Kasatkin and L.P. Pasechnik: Opt. Spectrosc. (USSR) 57 (1984) 6.

/ 6/ V.F. Masterov: Sov. Phys. Semicond. 18 (1984) 1.

/ 7/ V.A. Kasatkin, F.P. Kesamanly, V.G. Makarenkov, V.F. Masterov and B.E. Samorukov: Sov. Phys. Semicond. 14 (1980) 1092.

/ 8/ V.A. Kasatkin, F.P. Kesamanly and B.E. Samorukov: Sov. Phys. Semicond. 15 (1981) 352.

/ 9/ V.A. Kasatkin: Sov. Phys. Semicond. 19 (1985) 1174.

/10/ H. Ennen, U. Kaufmann, G. Pomrenke, J. Schneider, J. Windscheif and A. Axmann: J. Cryst. Growth 64 (1983) 165.

/11/ H. Ennen, G. Pomrenke and A. Axmann: J. Appl. Phys. 57 (1985) 2182.

/12/ H. Ennen and J. Schneider: J. Electron. Mater. 14A (1985) 115.

/13/ W.H. Haydl, H.D. Müller, H. Ennen, W. Körber and K.W. Benz: Appl. Phys. Lett. 46 (1985) 870.

/14/ K. Uwai, H. Nakagome and K. Takahei: GaAs and related compounds, Las Vegas USA, 1986 (Institute of Physics Conference Series Number 83, ed. by W.T. Lindley) 87.

/15/ K. Uwai, H. Nakagome and K. Takahei: Appl. Phys. Lett. 50 (1987) 977.

/16/ J. Wagner, J. Windscheif and H. Ennen: Phys. Rev. B30 (1984) 6230.

/17/ G. Aszodi, J. Weber, Ch. Uihlein, L. Pu-Lin, H. Ennen, U. Kaufmann, J. Schneider and J. Windscheif: Phys. Rev. B 31 (1985) 7767.

/18/ R. Kallenbach, H.J. Reyher, J. Unruh, A. Winnacker and H. Ennen: Proc. of the 14th Int. Conf. on Defects in Semicond. ICDS - 14, ed. by H.G. von Bardeleben, Materials Sciences Forum Vol. 10-12 (1986) 681.

/19/ V.A. Kasatkin, V.F. Masterov, V.V. Romanov, B.E. Samorukov and K.F. Shtel'makh: Sov. Phys. Semicond. 16 (1982) 106.

/20/ V.F. Masterov, V.V. Romanov and K.F. Shtel'makh: Sov. Phys. Solid State 25 (1983) 824.

/21/ A. Stapor, J. Raczynska, H. Przybylinska, A. Sienkiewicz, K. Fronc and J.M. Langer: Proc. of the 14th Int. Conf. on Defects in Semicond. ICDS-14, ed. by H.G.von Bardeleben, Materials Sciences Forum Vol. 10-12, (1986) 633.

/22/ H.D. Müller, H. Ennen, J. Schneider and A. Axmann: J. Appl. Phys. 59 (1986) 2210.

/23/ J. Wagner, H. Ennen and H.D. Müller: J. Appl. Phys. 59 (1986) 1202.

/24/ A.A. Gippius, V.S. Vavilov, V.V. Ushakov, V.M. Konnov, N.A. Rzakuliev, S.A. Kazarian, A.A. Shirokov and V.N. Jakimkin: Proc. of the 14th Int. Conf. on Defects in Semicond. ICDS-14, ed. by H.G. von Bardeleben, Materials Sciences Forum Vol. 10-12, (1986) 1195.

/25/ V.F. Masterov,V.V. Romanov, B.E. Samorukov and K.F. Shtel'makh: Sov. Phys. Semicond. 17 (1983) 596.

/26/ V.V. Ushakov, A.A. Gippius, V.A. Dravin and A.V. Spitsyn: Sov. Phys. Semicond. 16 (1982) 723.

/27/ H. Ennen, J. Schneider, G. Pomrenke and A. Axmann: Appl. Phys. Lett. 43 (1983) 943.

/28/ G. Pomrenke, H. Ennen and W. Haydl: J. Appl. Phys. 59 (1986) 601.

/29/ F. Bantiem, E. Bauser and J. Weber: J. Appl. Phys. 61 (1987) 2803.

/30/ R.S. Smith, H.D. Müller, H. Ennen, P. Wennekers and M. Maier: Appl. Phys. Lett. 50 (1986) 49.

/31/ H. Ennen, J. Wagner, H.D. Müller and R.S. Smith: J. Appl. Phys. 61 (1987) 4877.

/32/ K. Thonke: unpublished results

/33/ A.G. Dmitriev, L.F. Zakharenkov, V.A. Kasatkin, V.F. Masterov and B.E. Samorukov: Sov. Phys. Semicond. 17 (1983) 1201.

/34/ W. Körber, J. Weber, A. Hangleiter, K.W. Benz, H. Ennen and H.D. Müller: J. Cryst. Growth 79 (1986) 741.

/35/ H. Ennen: unpublished results

/36/ H. Ennen, G. Pomrenke, A. Axmann, K. Eisele, W.H. Haydl and J. Schneider: Appl. Phys. Lett. 46 (1985) 381.

/37/ W.T. Tsang and R.A. Logan: Appl. Phys. Lett. 49 (1986) 1686.

/38/ J.P. van der Ziel, M.G. Oberg and R.A. Logan: Appl. Phys. Lett. 50 (1987) 1313.