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INTERBAND EXCITATION INDUCED ABSORPTION BY DEEP IMPURITIES IN GaP

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Transient optical absorption at energies below the band gap in GaP crystals following pulsed interband excitation was observed. The additional absorption attained its maximum about 25 μsec after the excitation pulse and lasted about 100 μsec. The spectral dependence of the rise time and decay time of the absorption and that of the induced optical cross section were determined. The results suggest that the induced absorption is caused by several deep impurity levels, which are most probably due to Cu, being populated by the recombination of excited electrons.

1. INTRODUCTION

DEEP IMPURITY CENTRES in GaP have been investigated with particular emphasis on the recombination kinetics of carriers and optical cross-sections by various methods including photoconductivity [1], photocapacitance measurements [2], luminescence [3] and optical absorption [4]. We report here on optically induced transient absorption measurements in GaP crystals containing deep impurity levels. Interband transitions were excited by a short pulse from a pump laser and the subsequent rise and decay of the optical absorption at photon energies below the band edge were detected by monitoring the transmission with a cw probe laser. At low temperatures a long-lived induced absorption was observed which is attributed to optical transitions of electrons from deep impurity levels to the conduction band. The impurity centres are populated from the conduction band by electrons excited by the pulsed pump laser, thus the induced absorption is determined by the electron concentration in the impurity levels. Our results show that this pump and probe technique is suitable for studying the transient behaviour of the electron population in impurity levels within the band gap of GaP. This method is also applicable to non-radiative transitions whose kinetics cannot be studied by luminescence measurements.

2. EXPERIMENTAL

The experiments were performed on GaP crystals nominally doped with Zn acceptors [5]. Optical absorption in the visible and near infrared spectral range and luminescence measurements revealed the presence of the following impurities, with approximate concentrations given in brackets: Zn ($\leqslant 10^{17}\,cm^{-3}$), S ($> 10^{17}\,cm^{-3}$, O ($\simeq 10^{17}\,cm^{-3}$) and Cu ($\geqslant 10^{16}\,cm^{-3}$). The free carrier concentration at room temperature of the p-conducting material was less than $10^{17}\,cm^{-3}$.

The samples were immersed in pumped liquid helium at 1.6 K and excited by pulses of 3 nsec duration and 0.1 mJ pulse energy from a dye laser at photon energy $h\nu_p = 2.366$ eV, which is slightly larger than the indirect band gap $E_g = 2.35$ eV. The absorption coefficient of the samples at ν_p was $8\,cm^{-1}$. The employed probe sources were a c.w. Kr^+ laser emitting several lines at quantum energies from just below the band gap (2.336 eV) to the near infrared (1.498 eV) and a high pressure Hg-lamp suitably filtered to cover the photon energy range below $h\nu_s \approx 1.5$ eV. The probe beam was irradiated on the sample in the opposite direction to the pump beam. Both beams were slightly tilted to allow a geometrical separation of the probe beam from the specular reflected part of the pump beam. Scattered light at the frequency of the pump laser was eliminated by a double monochromator. The cross-sections of both beams were varied between 0.1 and 1 mm^2; the length of the overlap region of the beams at the entrance of the pump beam in the crystal was in the order of 1 mm. The transmission change of the probe beam intensity upon pumping the crystal was detected by a Si-photodiode with time resolution better than 1 μsec.

In an additional experiment interband transitions were also found at pump photon energies below the band gap due to a two-step optical process involving midgap energy levels well known for GaP from investigations of up-conversion fluorescence [6]. In the present case the excitation is presumably caused by oxygen impurities. This method of excitation allows homogenous pumping of a rather large sample volume. The behaviour of the transient absorption $\Delta\alpha$ was similar to the one step excitation case and will not be discussed separately.

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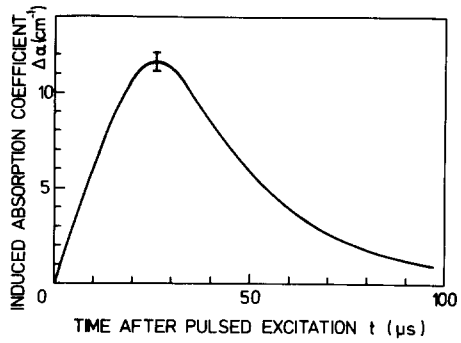

Fig. 1. Time dependence of induced absorption $\Delta\alpha$ in GaP for $E_p = 100\,\mu J$, $h\nu_p = 2.366$ eV and $h\nu_s = 1.916$ eV.

3. RESULTS

The typical transient behaviour of the interband excitation induced absorption $\Delta\alpha$ observed at quantum energies below the band edge is shown in Fig. 1. The negative logarithm ($-\ln \Delta T$) of the transmission change ΔT at $h\nu_s = 1.916$ eV, which is proportional to the average induced absorption $\Delta\alpha$ in the overlap volume of the pump and the probe beam, is shown as a function of time for 0.1 mJ pump pulse energy. The induced absorption evolves on a totally different time scale than the 3 nsec pulses. The absorption rises continuously when the pump pulse has already ceased attaining a maximum after about 25 μsec corresponding to an estimated $\Delta\alpha \approx 10\,\text{cm}^{-1}$, and decays with an apparent decay time of about 20 μsec. An analogous behaviour of the absorption was observed in the whole range of Kr^+ laser lines and also at $h\nu_s \geqslant 1.44$ eV as found from a measurement with the Hg-lamp and suitable optical filtering. On insertion of a 0.5 mm thick slice of GaAs as an optical low pass filter no induced absorption could be detected, which indicates a low energy limit for the induced absorption of about $h\nu_s = 1.44 \pm 0.05$ eV.

It was found that the induced absorption coefficient is independent of the probe laser power and also does not depend on the photon energy of the pump laser as long as pumping occurred above the band gap. For the lower quantum energies $h\nu_s$ (1.498 to 1.916 eV) $\Delta\alpha$ increases linearly with the pump pulse energy E_p, whereas at the larger ones ($h\nu_s = 2.182$ and 2.336 eV) a slightly superlinear relation $\Delta\alpha \propto E_p^{1.25}$ was found.

The apparent decay time of $\Delta\alpha$ was found to be independent of E_p and decreased with increasing probe photon energy $h\nu_s$. The rise time, however, and the time delay at which $\Delta\alpha$ reaches its maximum value, both increased with rising pump pulse energy E_p and decreased with increasing photon energy $h\nu_s$.

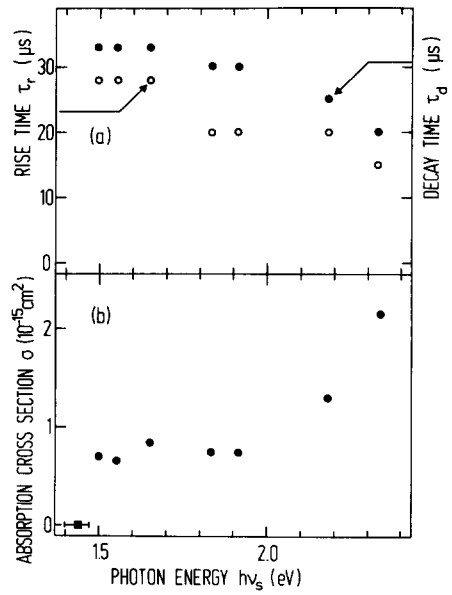

Fig. 2. (a) Rise time τ_r (○) and decay time τ_d (●), and (b) induced optical cross section as a function of probe laser photon energy $h\nu_s$. The square (■) denotes a measurement with a high pressure Hg-lamp. The error of the rise and decay times is about 5 μsec, the relative error of the optical cross-section about 30 percent.

4. DISCUSSION

Our result can be explained by assuming that, after pulsed interband excitation, electrons are trapped into deep centres within the time τ_r, and that the probe radiation is absorbed by excitation of a small fraction of the trapped electrons to the conduction band. τ_r is then the population time of the deep centres and also the rise time of the induced absorption. The majority of the trapped electrons recombines into the valence band with the decay time τ_d of the observed absorption.

We wish to point out that the occurrence of the induced absorption cannot be explained by indirect interband transitions involving the absorption of phonons produced by absorbing the pump pulse. In that case $\Delta\alpha$ should instantaneously increase with the pump pulse and the induced absorption should disappear below about 2.3 eV, i.e. the excitonic band gap diminished by the energy of phonons at the X-point of the Brillouin zone [7].

The transient behaviour of the additional absorption is determined by the recombination kinetics of the excited electrons. In order to obtain a coarse estimate of the time constants τ_r and τ_d we assume for the sake of simplicity exponential population and decay of the electron concentration in the deep centres. The absorption coefficient $\Delta\alpha$ then follows by convolution of the population (e^{-t/τ_r}) and decay functions (e^{-t/τ_d}):

$$\Delta\alpha \propto \left(\frac{1}{\tau_d} - \frac{1}{\tau_r}\right)(e^{-t/\tau_r} - e^{-t/\tau_d}) . \quad (1)$$

By fitting this function to the experimentally determined time dependence of the induced absorption we find that the decay time τ_d and the population time τ_r decrease with increasing $h\nu_s$ as displayed in Fig. 2(a). This result indicates that several deep impurity levels with different population and recombination times must be involved and that the recombination must occur at isolated donor–acceptor pairs.

We suggest that the induced absorption is due to Cu impurities [4] which cause several deep levels at 0.17, 0.52 ("*A*-centre"), 0.70 ("*B*-centre") and 0.8 to 0.9 eV above the valence band [2, 3]. Also the observed population time τ_r of the deep levels is of the same order of magnitude as the decay time of the red luminescence emitted by Cu–S pair emission, where the *A*-centre is involved [8]. Furthermore, photoconductivity measurements indicate that the lifetime of holes in GaP : Cu is not longer than 40 μsec [7] which is approximately equal to the decay times τ_d found in our experiment.

In the following we try to estimate the optical absorption cross-section. The absorption cross-section for the probe radiation is given by

$$\sigma = \Delta\alpha/C^* = \frac{\Delta\alpha}{\beta n} \quad (2)$$

where C^* is the concentration of populated deep levels, and n is the density of electrons excited by the pump pulse. The coefficient β is the fraction of the electrons recombining via the deep centres. A lower limit for β can be estimated to be of the order of 1/50 because photoluminescence measurements on our sample show that about 1/50 of the excited electrons relax radiatively via deep levels. Then the yielding cross-section σ is found to be of the order of 10^{-15} cm^2, similar to the value of Grimmeiss *et al.* [4]. This confirms our estimate of β, indicating that radiative recombination is dominant. If most of the unaccounted transitions occurred non-radiatively [9] via copper, β could have the upper limit of 1 and σ would be of the order of 10^{-17} cm^2. The spectral dependence of σ is shown in Fig. 2(b). σ rises at 1.45, and between 1.5 and 1.9 eV it remains almost constant, then it rises again. This shows that at least two deep levels must contribute to the induced absorption.

In equation (2) for the absorption cross-section a linear dependence of $\Delta\alpha$ on the pump pulse energy E_p is presumed. The superlinear behaviour observed with $h\nu_s$ close to the band gap may be explained by two-step excitations via the deep impurity oxygen being present in the sample [6].

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REFERENCES

1. R.G. Schulze & P.E. Petersen, *J. Appl. Phys.* **45**, 5307 (1974).
2. H.G. Grimmeiss, *Semiconductor Optoelectronics* (Edited by M.A. Herman), p. 33. Warsaw (1980).
3. H.G. Grimmeiss, B. Monemar & L. Samuelson, *Solid State Electron.* **21**, 1505 (1978).
4. H.G. Grimmeiss & H.O. Ottosson, *Phys. Status Solidi (a)* **5**, 481 (1971).
5. The crystals were supplied by Wacker Chemietronic, 8263 Burghausen/Inn, West Germany.
6. A. Schindler, K. Bindemann & K. Kreher, *Phys. Status Solidi (b)* **59**, 439 (1973).
7. P.S. Dean & D.G. Thomas, *Phys. Rev.* **150**, 690 (1966).
8. K. Moser, R. Baumgartner & W. Prettl (to be published).
9. C.H. Henry & D.V. Lang, *Phys. Rev.* **B15**, 989 (1977).