PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980 J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 255–258

# CALORIMETRIC ABSORPTION SPECTROSCOPY (CAS) OF GaP:N,S

A. Bubenzer<sup>(a)</sup> and D. Bimberg<sup>(b)</sup>

- (a) Fraunhofer-Institut für Angewandte Festkörperphysik, Eckerstr. 4, D-7800 Freiburg, W.-Germany
  (b) Institut für Halbleitertechnik der RWTH,
- (b) Institut für Halbleitertechnik der RWTH, Sommerfeldstrasse, D-5100 Aachen, W.-Germany

A new, simple and highly sensitive spectroscopic method (CAS) for direct detection of phonons emitted via nonradiative recombination processes of charge carriers bound to defects or impurities in solids is demonstrated. Electronic levels of these centers are populated by resonant excitation with monochromatic light. The phonons emitted during recombination are detected with a low temperature calorimeter. CAS spectra of N and S doped GaP are compared with standard absorption and luminescence spectra. The internal quantum efficiency of the (N,X) J = 1 $\rightarrow$  O radiative recombination is determined as being close to 100 %. The minimum absorption coefficient which could be detected with the samples used here was < 10<sup>-5</sup> cm<sup>-1</sup>.

### I. Introduction to the Method

An externally excited solid can relax to thermal equilibrium by emission of either photons or phonons. Highly sophisticated spectroscopic techniques to detect and to analyse emitted photons are well established. No spectroscopic techniques of similar versatility and sensitivity exist to date for the detection and analysis of phonons. Yet the desirability of a phonon spectroscopy is highly recognized e.g. for investigations of shallow and deep impurities or defects in semiconductors. Such investigations would be of interest from a fundamental point of view to provide information about the electronic structure of such centers, their interactions with each other and with the lattice and for many applications, since e.g. the performance of optoelectronic devices like LED's or fast infrared detectors depends strongly on the presence and the properties of defects and impurities. With this contribution calorimetric absorption spectroscopy (CAS) - a further development of the well known calorimetry - is introduced as a spectroscopic technique to investigate phonon emitters. This technique appears to be simpler and more sensitive than the recently proposed acoustooptic spectroscopy [1].

The principles of CAS are discussed first. Then some results of a comparative study of CAS, absorption and emission spectra of N and S doped GaP crystals at low temperatures are presented to demonstrate the sensitivity of the method. It is found that the ex-

#### A. BUBENZER and D. BIMBERG

citon bound to isoelectronic nitrogen has an internal quantum efficiency of close to 100 %.

In CAS a pulsed monochromatic light beam is absorbed by some resonant state in a solid. During relaxation to thermal equilibrium phonons are emitted. Part of the phonons are transmitted to a calorimeter and give rise to a voltage signal. The wavelength dependent change of the voltage is measured. Thus the method is the equivalent to one of the most modern and elegant optical techniques, excitation spectroscopy, with the sole difference that the signal is an integral measure of the phonons.

The energy Q absorbed from a light pulse of intensity  $I_{o}$ , wavelength  $\lambda$ , and duration  $\Delta t$  is  $I_{o} (1 - R) (1 - \exp(- \lambda d)) \Delta t$ 

$$Q = \frac{0}{1 - R \cdot \exp(-\alpha d)}$$
(1)

where  $\checkmark$  ( $\lambda$ ) is the absorption coefficient, d the thickness of the sample and R the reflection coefficient. For values  $\checkmark$  d  $\ll$  1, typical for impurity absorption in not too thick samples, (1) simplifies to

 $Q = I_{Q} \ll d \Delta t , \qquad (2)$ 

The part  $\eta Q$  of the absorbed energy is reemitted in the form of photons. The remaining part  $W = Q (1 - \eta)$ , where  $\eta$  is the internal quantum efficiency for radiative recombination, is emitted in the form of phonons. The quantum efficiency  $\eta$  equals  $\tau_t / \tau_r$  where the experimentally determined total lifetime  $\tau_t$  depends on the radiative and nonradiative lifetimes  $\tau_r$  and  $\tau_{nr}$  via  $(\tau_t)^{-1} = (\tau_r)^{-1} + (\tau_{nr})^{-1}$ .

For small quantum efficiencies  $\mathfrak{N} \approx 0$ ,  $\mathbb{W} \approx \mathbb{Q}$ . The number of emitted phonons is then a sole function of  $\mathfrak{d}$ . Consequently the absorption coefficients of strongly "nonradiative centers" can be determined precisely without using a photon detector as far as  $\mathfrak{d}$  is nonvanishing.

For  $\eta > 0$  W depends on two variables,  $\checkmark$  and  $\eta$ . If  $\checkmark$  is measured independently,  $\eta$  can be determined and a complementary measurement of  $\gamma_{\pm}$  yields then independent values of  $\gamma_{\Gamma}$  and  $\gamma_{\Pi\Gamma'}$ lifetimes which are difficult to determine otherwise. Finally a direct comparison of the relative absorption and CAS spectra of <u>different</u> centers, at least one having  $\eta > 0$ , leads to a direct determination of  $\eta$  of the centers with  $\eta \neq 0$  already <u>without</u> quantitative calibration of Q. An example for this already more sophisticated but experimentally simple application of CAS will be given.

The sensitivity of CAS depends mainly on the sensitivity of the calorimeter. The temperature rise of the calorimeter is given by

$$\Delta T = \frac{W}{m_{s}c_{s} + m_{c}c_{c}}$$

where  $m_{c}$ ,  $m_{c}$ ,  $c_{c}$  and  $c_{c}$  are the masses and specific heats of sample s and calorimeter c, respectively. Since the specific heat of solids drastically decreases with temperature the sensitivity can be increased considerably by cooling down to a few K (2). Low temperature calorimetry is several orders of magnitude more sensitive than room temperature calorimetry, not only due to the decreased specific heat, but also because small temperature differences can be measured more accurately at low temperatures. Most conveniently the change of the resistance R of a sensor with temperature T is measured, using sensors like carbon resistors with large and nonlinear dR/dT. A simple decrease of temperature e.g. from 4.2 K to

1.5 K can thus lead to further improvements of the sensitivity by orders of magnitude. The CAS experiments described in Section II where performed in the following way. The samples were suspended in the evacuated sample chamber of an optical He<sup>4</sup> cryostat and 1.5K. The thermal contact of the mostly kept at a temperature of sample to its environment has to be kept as low as possible. As thermal sensors carbon resistors were used.With increasing temperature their resistance decreases. Typically the temperature rise is a few mK leading to resistance variations of the order of  $k \mathfrak{A}$  . The change of the voltage drop across the resistors following the emission of phonons in the sample was monitored with a transient recorder. In order to avoid false signals due to light scattering the carbon resistors are surrounded by radiation shields and are thermally connected to the sample by thin copper wires. As light sources we used an argon pumped dye laser as well as a high pressure mercury lamp and a grating monochromator with spectral bandwidth of 0.3 A.

# II. CAS of GaP:N,S as example

A number of nominally undoped epitaxial and bulk grown GaP samples were investigated to demonstrate the merits of CAS. An inspection of the lumi-



nescence spectra showed that all samples contained N and S as impurities. Figure 1 shows a typical luminescence spectrum of a bulk sample. and B The A lines are due to the decay of the J = 1 and 2 states of the N bound exciton [3], the origin of the broad line is discussed in Refrence[4] and the C-line at 5367 Å is due to the decay of the sulphur bound exciton [5]. In contrast to the CAS and absorption spectra which are superimposed in Fig. 2 the relative intensity



of the different luminescence lines varied with excitation.A key result is certainly the observation of the very sharp structure in the CAS spectrum showing not only the  $J = 0 \rightarrow 1$  transition of (N,X)and the  $J = 1/2 \rightarrow 3/2$  transition of the  $(S^{\circ}, X)$  but also the  $J = 0 \rightarrow 2$ transition of (N,X) not observed in the absorption. This is explained by a different quantum efficiency and thus phonon emissivity of the J = 1 and 2 bound exciton states.Whereas the J = 2 state has  $\eta$  close to zero,  $\eta(J = 1) > 0$ .The ratio of the A and C lines in CAS (2:1) and absorption (6:1) differs strongly.The quantum efficiency of  $(S^{\circ}, X)$  is close to zero.All absorbed power is transferred into phonons.For comparison only 1/3 of the power absorbed by nitrogen at the wavelength of the  $J=0 \rightarrow 1$  transition is transferred into phonons. A. BUBENZER and D. BIMBERG



The radiative quantum efficiency of this process is thus 67%.We should note that this is the external quantum efficiency of the sample under investigation. The internal quantum efficiency of the  $J = 1 \rightarrow 0$  recombination can be estimated to be close to 100% from these results in agreement with more indirect older determinations.

It should further be noted that the 5356 Å band is neither observed in the CAS nor in the absorption spectrum.

Fig.2 CAS and absorption spectra of GaP:N,S

The sensitivity of CAS for the present system was estimated using the same sample shown in Figs. 1 and 2 by reducing the optical power to a point where no CAS signal could be detected any more. Using a Dye-laser with a power reduced to a few nW and a sample of a thickness of 200µm and a mass of 20 mg a sensitivity of  $< 10^{-6}$  cm<sup>-1</sup> was obtained. This is certainly not yet the ultimate what can be achieved with CAS.

#### Acknowledgements

We are indebted to the hospitality of the Max-Planck-Institut für Festkörperforschung in Stuttgart where the experimental part of the work was done, to H. Tews and H. Breitschwerdt for taking the luminescence and absorption spectra, to P.J. Dean for helpful comments and to M.S.Skolnick for the gift of one of the crystals.

### References

- A. Rosencwaig: Advances in Electronics and Electron Physics, Vol. 46 (1978) 207, L. Marton ed., Academic Press.
- 2) A. Bubenzer, S. Hunklinger and K. Dransfeld: J. Non-Cryst. Solids, in print (1980)
- 3) D.G. Thomas, J.J. Hopfield and C.J. Frosch: Phys. Rev. Lett. 17 (1965) 857
- 4) J.L. Merz, R. A. Faulkner, and P. J. Dean: Phys. Rev. 188 (1969) 1228 .
- 5) P.J. Dean: Phys. Rev. 157 (1967) 655