# «Spectroscopic Study, (Raman-Luminescence), of III-V and II-VI Bulk and Layered Semiconducting materials»

## **Research Team**

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## 1. Introduction

Bulk compounds and layered (micro- and nano-) structures based on the II-VI and III-V semiconducting groups, have been studied, by optical spectroscopy methods such as Raman scattering (RS), Photo-Luminescence (PL) and Photo-Reflectance (PR), as far as it concerns their lattice dynamical properties, related piezoelectric and electro-optic effects, coupled modes of the optical phonons with the plasma excitations, as well as the elastic deformation of the heterostructures and the observed strain relaxations.

## 2. PHASE A: Study of II-VI and II-VI/III-V materials and structures

2.1 Elastic strains and piezoelectric fields (PZEF) on CdTe

(bulk and quantum-well structures)

The subject of the first part of phase-A is the study of the influence of elastic strains to the spectroscopic characteristics of the materials. Moreover, in the case that the semiconducting materials exhibit, under elastic strain, non-screened piezoelectric field (PZEF), the influence of this field on the phonon frequencies is also studied. This research has been carried out in cooperation with the "Institute of Electronic Structure and Lasers" (FORTH, Crete) and the "Département de Research Fondamentale sur la Matière

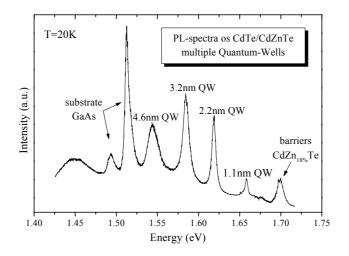


Figure 1. Photoluminescence-spectra of multiple quantum-well

Condensée", CEA/Grenoble, SP2M, F-38054 (Grenoble, France), through Dr. N. Pelekanos, (Assoc. Professor, University of Crete). The results of this research have been published in the form of an extended regular article in Phys. Rev. B, by Stergiou et al., [1]. In this article, the spectroscopic study (mainly Raman, but also Luminescence), has been presented, for bulk CdTe samples under elastic strain at low temperature (80K), as well as for CdTe/CdZn(Mn)Te quantum wells (QWs), grown along the crystallographic directions [001] and [111], (see Fig.1, for PL spectra of multiple QWs). In the latter systems (QWs), the wells (CdTe) are under bi-isotropic elastic strain, due to their under-critical thickness, (of the order of few nanometers), and their lattice misfit with respect to the barriers (CdZn(Mn)Te) and the supporting buffer-substrate

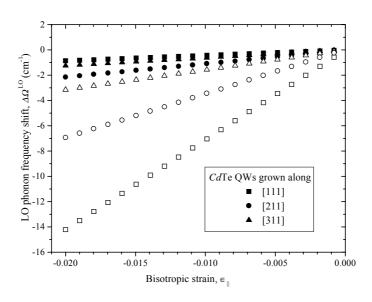


Figure 2 LO-frequency shifts vs. strain, for QWs grown along several directions, considering zero (open symbols) and non-zero (solid symbols) piezoelectric field.

combination. In the CdTe/CdZn(Mn)Te quantum wells grown along the crystallographic direction [111], piezoelectric fields are also developing, which are not screened due to the low carrier concentration and the nano-thickness of the layered structures. Combining the Raman data of the bulk and the layered nanostructures, the deformation potentials (DPs) due to the elastic strain as well as due to the piezoelectric field are, finally, obtained. Using the obtained DPs, it is shown that the piezoelectric field induces a non-negligible contribution to the frequency-change of the lattice vibrations. The PZEF-induced contributions to the change of the phonon frequencies, expected for the elastically strained QWs, grown along the lower symmetry crystallographic directions [211] and [311], were also calculated, on the base of the obtained DPs, (see Fig.2). The values obtained for the DPs of CdTe are compared with the trends and the systematic behaviour of other materials of the same compoundsemiconductors family, while the phonon DPs, due to elastic strain, for the polycrystalline and the textured CdTe, are also calculated.

## 2.2 Study of ZnSe-based layered structures

The subject of the second part of the phase-A is the study of thin ZnSe-based layered structures of the type of  $ZnS_{1-x}Se_x$  and  $ZnSe_xTe_{1-x}$ , with variable composition (x), grown over different substrates such as GaAs and InP. The aim of this research is the characterization of the above-mentioned layered structures as far as it concerns their real composition and its probable variation in micro- and macro-scopic scale, the elastic strain distribution and their degree of relaxation, as well as the characteristics of the carriers in the interlayer of the films. This research has been carried out in collaboration with M. Strassburg, M. Strassburg, O. Schulz, U. W. Pohl, A. Hoffmann, D. Bimberg,, from the Technical University of Berlin, (Institut fuer Festkoerperphysik), where the samples, used in this work, were grown. The results of this work have been published in the form of one regular article in "Thin Solid Films", [2], two regular articles in the "Journal of Crystal Growth", [3, 4], and have been presented in the E-MRS 2002 Spring Meeting, (Strasburg, June 18-21, 2002), [5].

In the first publication, by Kontos et al., [Ref.2], the N-doped ZnSSe epilayers, grown over GaAs-substrate with monomer and dimmer Se-precursors, are studied. The structural characteristics of the epilayers are determined by the combined analysis of X-ray diffraction data and the Raman frequencies of the, ZnSe-type and ZnS-type, vibrational LO and TO modes.

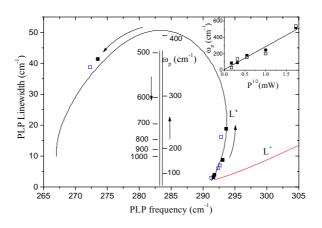


Figure 3. Frequency-width correlation of the GaAs-PLP mode

From this investigation, it is concluded that optimal structural properties of the epilayer are obtained with the monomer Se-precursor. The Raman spectra exhibit coupled Plasmon-LO-Phonon (PLP) vibrational modes from the GaAs interlayer. Monitoring the correlation between the width (FWHM) and the frequency of the PLP modes, for two different samples and under variable excitation power, it is proposed that the PLP collective excitations are due to photo-excited carriers. The detailed changes of their characteristics are analyzed on the base of band-bending effects close to the substrate-epilayer interface.

In the second publication, by Kontos et al., [3], thin ZnSeTe layers, (thickness of 350 nm), MOVPE-grown over InP-substrate, are studied with X-ray diffraction and Raman spectroscopy. The combination of XRD and Raman data, together with a model

which assumes: (i) partial relaxation of the elastic strain, and (ii) deviation from the nominal composition, allows the determination of those two parameters, (partial strain relaxation and real stoichiometry). The relative variation of those to effects has been also studied as a function of the growth conditions and by the insertion of an intermediate buffer layer, between the substrate and the epilayer. The conclusions of this study are leading to the determination of the optimum growth conditions, in such a way as to minimize the divergence from the nominal stoichiometry and the relaxation of the elastic misfit strains of the epilayer.

In the third publication, by Strassburg et al., [4], thin ZnSeTe layers, MOVPEgrown over InP-substrate, are studied, as far as it concerns the influence of the phosphorous-doping. The influence, on the epilayer, of the molecular ratio in the vapor phase, as well as the use of a ZnCdSe buffer layer is presented. The dependence of the hole concentration on the degree of P-incorporation and on the composition of the layer has been revealed. The first- and second-order micro-Raman spectra of ZnSeTe are measured, and their analysis is in accordance with an one-mode behavior of the ternary compound. The influence of the ZnCdSe buffer layer, on the homogeneity of the ZnSeTe epileyer, was studied by means of the micro-Raman spectra.

## 3. PHASE B (Study of II-VI and III-V semiconducting compounds)

### 3.1 Anharmonic study and Faust-Henry coefficient of CdTe

The subject of this research is the study, by means of Raman spectroscopy, of the crystallodynamic properties of CdTe, as a function of temperature, (in the range of 20-300K), and the excitation energy. The temperature dependence of the peak frequency and the width, (FWHM), of the Raman scattering bands from the optical lattice

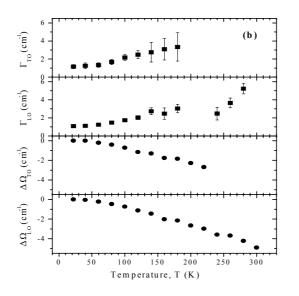


Figure 4 Anharmonic effects on optical phonons

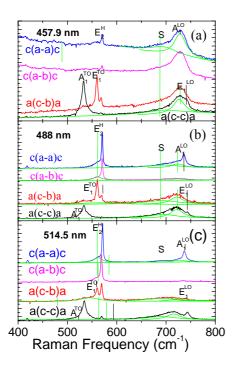
vibrations, (LO and TO) of the Brillouin-zone center,  $(q\approx 0)$ , are mainly attributed, on the base of an anharmonic analysis presented in this work, to effects related with decay

of phonons from the center of the Brillouin zone to phonons related to critical points far from the center of the Brillouin zone. The LO/TO intensity ratio is also studied as a function of the temperature and the excitation energy. The further analysis of this ratio can lead to the determination of the Faust-Henry coefficient,

$$C = \left(\frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2}\right) \left\{ 1 - \left[ \left(\frac{n_{TO} + 1}{n_{LO} + 1} \right) \left(\frac{\omega_{TO}^S}{\omega_{LO}^S}\right)^4 \left(\frac{\omega_{LO}}{\omega_{TO}} \right) \left(\frac{\rho_{exper.}}{\rho_{theor.}}\right) \right]^{1/2} \right\}^{-1}$$
(1)

which is a measure for the relative contribution of the lattice and the electrons to the linear electro-optic tensor. This analysis, for CdTe at 20K, gives an almost constant value of the Faust-Henry coefficient, for the whole range of the excitation-energy investigated (1.49 - 1.54 eV). The analysis has been completed and the work is in the form of a manuscript almost ready to be submitted, by Stergiou and Raptis [6].

## 3.2 Study of InGaN/GaN heterostructures



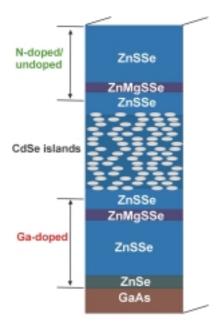
**Figure 5.** m-Raman spectra of InGaN/GaN, under various excitation wavelengths and polarizations.

publication, by Kontos et al., [7].

The subject of this work is the study of In<sub>x</sub>Ga<sub>1-x</sub>N/GaN heterostructures grown over an Al<sub>2</sub>O<sub>3</sub> substrate. Samples of four different compositions, x=0.10, 0.15, 0.19, 0.196 and 0.265, have been measured with micro-Raman spectroscopy, in backscattering configuration along different two crystallographic orientations, namely, the growth orientation ( $[c(aa)\overline{c}], [c(ab)\overline{c}]$ ), and a perpendicular cleavage one  $[a(cc)\bar{a}]$ , and  $[a(cb)\bar{a}]$ , with simultaneous application of the polarization selection rules. All the observed Raman scattering bands were identified and assigned to lattice vibrations of either the GaN substrate or the InGaN substrates, in accordance with the literature. The frequency shifts of the observed Raman bands, relative to the corresponding bands of the bulk materials, have been used in order to estimate the elastic strain of the InGaN epilayer. The analysis and evaluation of the data have taken into account independent measurements of Xray diffraction and Rutherford backscattering, in order to obtain strain and relaxation values consistent with the different methods. The work has been completed and submitted for

In order to explain any difference between the strain and relaxation values obtained using different methods, preliminary photoreflectance measurements have been carried out. The related first draft, on the preliminary photoreflectance measurements, [Photoreflectance measurements of the InGaN/GaN/sapphire heterostructures, A.G. Kontos, Y.S. Raptis, N. Pelecanos, A. Georgakilas, (in preparation)], is in a preliminary stage and needs further elaboration in the form of complimentary measurements and more extented analysis.

## 3.3 Study of CdSe/ZnSSe/GaAs quantum islands



**Figure 6.** Schematic diagram of the heterostructure and the self-organized CdSe quantum islands

CdSe quantum islands are studied, combining Xray diffraction and Raman spectroscopy. These quantum islands, which are very good candidates as active medium for semiconductor lasers, are formed by a self-organizing procedure, during the evaporation of one molecular mono-layer over a thin ZnS<sub>0.15</sub>Se<sub>0.85</sub> layer. The result of this selforganization is the spontaneous formation of Cdrich CdZnSe quantum islands with typical dimensions of 3-5 nm. The Raman study of such sequential systems was done with different excitation frequencies, in order to monitor spectroscopic indications of the quantum islands. In addition to the scattering bands originating from the layered constituents of the system, a scattering band in the range of 226 cm<sup>-1</sup> has been observed, which could be attributed to the scattering from the lattice vibrations of the quantum islands, depending on the Zn-composition of these island. The, up to now, results of this work are in the form of a reference report [Structural study of CdSe/ZnSSe/GaAs quantum islands laser structures, A.G. Kontos, Y.S. Raptis, M. Straßburg, U.W. Pohl, D. Bimberg].

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**3.** A. G. Kontos, Y. S. Raptis, M. Strassburg, U. W. Pohl, "Epitaxy and structural characterization of ZnSeTe Layers grown on InP substrates", *J. of Crystal Growth*, **247**, 17-22 (2003).

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**6.** V. C. Stergiou and Y. S. Raptis, "Anharmonic Effects and Faust-Henry coefficient of CdTe, studied in the vicinity of the Energy Gap" (*to be submitted*).

**7.** A.G. Kontos, Y.S. Raptis, N. Pelecanos, A. Georgakilas, E. Bellet-Amalric, D. Jalabert "m-Raman Characterization of InGaN/GaN/Al<sub>2</sub>O<sub>3</sub> Heterostructures", *Phys. Rev. B*, (submitted).