Micro-Raman study of photoexcited plasma in GaAs bevelled structures

R. Srnanek a,*, G. Irmer b, J. Geurts c, M. Lentze c, D. Donoval a, B. Sciana d, D. Radziewicz d, M. Tlaczala d, M. Florovic a, I. Novotny a

a Department of Microelectronics, Slovak University of Technology, Ilkovicova 3, 81219 Bratislava, Slovak Republic
b Technische Universität Bergakademie Freiberg, D-09596 Freiberg, Germany
c Physikalisches Institut, Universität Würzburg, D-97074 Würzburg, Germany
d Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology, 50-237 Wrocław, Poland

Received in revised form 8 September 2004; accepted 8 September 2004
Available online 13 October 2004

Abstract

The properties of the photoexcited plasma in n-GaAs and its influence on micro-Raman spectra were studied on bevelled structures. The modes of the photoexcited free-carriers plasmon–LO–phonon (PLP) coupling have been detected in the surface depletion layer at room temperature in continuum wave (CW) mode. The strong modifications of the intensities of TO–phonon and LO–phonon modes were observed along the bevel. They were discussed in terms of scattering by PLP coupling. The dependence of the ratio of the intensities of TO–phonons and LO–phonons was linear along the bevel in the region of the surface depletion layer. The first derivative of this dependence is a characteristic value for the corresponding doping concentration. Five Si-doped GaAs layers with different doping levels were analyzed in this way to obtain a calibration function for determining the doping concentration profile in the very thin GaAs layers.

© 2004 Elsevier B.V. All rights reserved.

PACS: 78.30. Fs; 68.55.Ln; 73. 20 Mf

Keywords: Micro-Raman; GaAs; Bevel; Photoexcited plasma; Plasmon–LO–phonon coupling

1. Introduction

GaAs is a suitable semiconductor material for many types of microelectronic and optoelectronic devices. Good knowledge of the physical properties of this material and in particular of the generation and dynamics of photoexcited carriers may provide a valuable insight for the design and development of high performance optoelectronic devices. Steady-state CW studies offer also a good possibility to observe the properties of photoexcited carriers [1–4].

* Corresponding author. Tel.: +421 2 60291653; fax: +421 2 65423480.
E-mail address: rudolf.srnanek@stuba.sk (R. Srnanek).
The first observation of light scattering by the photoexcited plasmon–LO–phonon (PLP) mode in III–V semiconductors was reported in GaP [4]. Subsequently, extensive studies of light scattering by single-particle and collective excitations of the electron–hole plasma were carried out in InP [5] and GaAs [6]. The light scattering by collective excitations of a photoexcited plasma in CW conditions was observed only when a GaAs layer was buried between the confining AlGaAs layers [1]. This fact was attributed to the high surface recombination velocity of electrons at free GaAs surfaces which is highly reduced at the AlGaAs/GaAs interface. In high purity GaAs, $L_+$ and $L_-$ modes of PLP coupling were observed using pulsed Ar or Kr lasers of very high power density at low temperatures [7]. The interaction of photoexcited electron–hole plasma with impulsively excited (femto-second range) coherent longitudinal optical phonons in GaAs was investigated via time-resolved second-harmonic generation [8] and by pico-second Raman scattering [9]. The coherent LO–electron and LO–hole coupling modes were observed and investigated in real time.

From the analysis of the results published during the last two decades (e.g. [1,5,10]), it is known that the modes of coupling between LO–phonon and photoexcited plasma in n-GaAs were not confirmed until yet at room temperature (RT) and under CW conditions. They were observed as spectral broadening of the LO band. In our work, we present the observation and study of the modes of this coupling in depletion layer of the bevelled n-GaAs structures at above conditions. The photoexcited electron–hole plasma in the GaAs depletion region is separated due to the built-in electric field, which allows to detect and to study these modes.

3. Results and discussion

In Fig. 1a, micro-Raman spectra taken from the bevelled Si-doped GaAs layer at four positions 1–4 are shown. The positions are labelled also on the schematic cross-section of the bevel in Fig. 1b. In Fig. 1b the carrier-free layer (depletion layer) under the surface is drawn. It is called a surface depletion layer. It was created due to attracting the free electrons from ionized Si atoms to the unsaturated atomic bonds at the surface. We assume an abrupt step-like transition from zero carrier concentration in the depletion layer to the bulk carrier concentration in GaAs:Si layer (Schottky’s approximation). Exact calculation of the surface electric field takes into account the finite penetration depth of the bulk carriers into the depletion layer due to their thermal energy. By this effect the step in the carrier density is spread to a finite width of the order of the effective Debye screening length [12]. This leads to a change of the surface electric field, which, however, is so small that it can be neglected for our considerations. By label “SCR” the space charge region at the UD GaAs and GaAs:Si interface is designed. It was created by diffusion of free electrons from the doped GaAs:Si layer to the UD GaAs layer. The doping concentration of the used GaAs:Si layer is $4 \times 10^{18}$ cm$^{-3}$ and we assume the full ionization of impurities. In Fig. 1a we see strong changes in Raman intensities detected at the

2. Experimental

Five different Si-doped GaAs structures grown by metal organic vapour phase epitaxy (MO VPE) on semi-insulating (0 0 0) GaAs substrates were used for experiments. The structures consist of a 500-nm thick Si-doped GaAs layer grown on a 1-μm thick undoped (UD) GaAs buffer layer. The doping concentrations were as following: $1 \times 10^{17}$, $5 \times 10^{17}$, $1.8 \times 10^{18}$, $2.8 \times 10^{18}$ and $4 \times 10^{18}$ cm$^{-3}$. The bevels were prepared by wet chemical etching in $H_3PO_4/H_2O_2/H_2O$ etchant. The value of the bevel angle $1.43 \times 10^{-4}$ rad was identical for all five structures. The details of bevel structure preparation were published elsewhere [11]. Micro-Raman spectra were measured using a 514.5 nm line of Ar ion laser in backscattering geometry at RT. Polarization of the incident laser light was parallel to [1 1 0] direction of the sample. The laser beam was focused by a microscope lens yielding to a spot size with diameter about 1–2 μm. Power density of about 60 kW/cm$^2$ was used in the experiments. Micro-Raman spectra were taken along the bevel with the average step of 10 μm. In the whole paper, by expression “along the bevel”, we mean the scanning of the laser spot upwards on the bevel surface, i.e., from low to high values of the bevel length. The presented spectra are shown after baseline correction.
frequency positions of LO–phonons and TO–phonons (shortly denoted as LO and TO intensities), decrease of LO and increase of TO intensities. These changes appear only when a high power density (60 kW/cm²) laser irradiation generating the high concentration of photoexcited-free carriers is used. By using a low power density (<1 kW/cm²) no differences in Raman spectra in positions 1–3 were detected. In position 1, the laser spot is placed on UD GaAs layer and therefore the measured Raman spectrum is the well-known characteristic spectrum of this type of material: LO peak at 292 cm⁻¹ of high intensity and TO peak at 268 cm⁻¹ of low intensity. TO peak in backscattering method is normally forbidden, but its small intensity can be attributed to a large collection angle of the objective of the microscope. In positions 2 and 3 the laser spot is placed on the surface depletion layer. A high decrease of LO intensity and remarkable increase of TO intensity are observed. These changes are caused by the influence of the modes of the coupling of the LO–phonon with the photoexcited plasma of the free electrons and holes (it will be explained later). In position 4, the laser spot is placed on the thick Si-doped GaAs layer. The corresponding spectrum is the well-known spectrum of scattering in highly n-doped GaAs, with L⁺ and L⁻ modes of PLP coupling of the free electrons coming from ionized Si atoms. The LO–phonon peak is coming from scattering of light in the surface depletion layer.

To study the changes in the Raman spectra it is suitable to evaluate the ratio of TO and LO intensities \(\frac{I_{\text{TO}}}{I_{\text{LO}}}\) due to the fact that LO intensity is influenced by the quality of the surface and the ratio partly compensates this fact. Otherwise, this ratio is proportional to the doping concentration [11]. In Fig. 2 the ratio \(I_{\text{TO}}/I_{\text{LO}}\) evaluated along the bevelled structure containing Si-doped GaAs layer with concentration of \(4 \times 10^{18} \text{cm}^{-3}\) is drawn. For further analysis this dependence was studied in four regions: I–IV, designed also in Fig. 1b.

Region I is characterized by a constant and small value of the ratio \(I_{\text{TO}}/I_{\text{LO}}\). In this region the micro-Raman spectra are very similar to those obtained using a low incidence power on UD GaAs, i.e., a high intensity of the LO–phonon peak and a very low intensity of the TO–phonon peak. By detailed inspection we can observe the differences in spectra

![Fig. 1](image1.png)

![Fig. 2](image2.png)
when using a high incidence power: small LO shift (about 1.0 cm\(^{-1}\)) to higher energies and its small broadening (about 2 cm\(^{-1}\)) which is consistent with the published results \[13\]. This fact was explained by coupling of photoexcited plasma with LO–phonon (PE–PLP coupling). Uncovered GaAs is characterized by an enormous surface recombination velocity \[9\]. Due to this fact most of the photoexcited electrons are attracted to the surface, and therefore only a small of the rest of these electrons are coupled with LO–phonon and create PE–PLP modes. Their concentration is about \(1 \times 10^{17} \text{ cm}^{-3}\), which causes the Raman shift of the higher energy mode of PE–PLP coupling \[9,13\] very close to the LO–phonon peak. The higher shift of this mode (at 323 cm\(^{-1}\)) was observable only using a very high incident power \[7\]. Additionally, by using a high incidence power we have observed a small increase of the ratio \(I_{\text{TO}}/I_{\text{LO}}\) (about 1\%) in region I. This is due to the fact that in the volume where the scattering due to PLP coupling takes place, scattering by LO–phonon is not present. Hence for a high incident power the observed LO intensity is lower than theoretically expected value.

In region II, the laser spot is scanned along a part of the bevel structure with presence of the surface depletion layer. The dependence in this region is linear as observed for all examined structures. There is a discontinuity observed between regions I and II caused by the interface between the UD GaAs layer and the surface depletion layer. Those two layers have different properties and therefore the dependence in this part is characterized by a strong increase of the value of \(I_{\text{TO}}/I_{\text{LO}}\). The discontinuity in the dependence designed with dotted line can be better seen in zooms in Figs. 3a and 5a.

Region III represents the part of bevel localised to SCR in the scattering volume. Due to the high dispersion of the \(I_{\text{TO}}/I_{\text{LO}}\) ratio it is not possible to determine the nature of the dependence in this region exactly. The dependence inclines to a constant value and we have designated this fact by the dotted line in Fig. 3a.

Region IV represents the part of bevel, which corresponds to the highly doped part of the GaAs layer in the scattering volume. In the upper part of the bevelled sample the laser light penetrates into both depletion and the GaAs:Si layers with high concentration of free electrons from ionized Si atoms. The \(I_{\text{TO}}/I_{\text{LO}}\) ratio in this region strongly increases due to an increased intensity of the L\(_{\text{mode}}\) mode, which is very close to TO position. Then it saturates to a maximum value due to the increased thickness of the doped layer, which exceeds the probing depth of the used laser (50 nm).

To perform a more detailed study of the processes of photoexcitation in the bevelled samples, Fig. 2 was magnified and re-plotted to Fig. 3a. In Fig. 3b and c there are corresponding dependences of \(I_{\text{TO}}\) and \(I_{\text{LO}}\) intensities at the same positions on the bevel as for the dependence \(I_{\text{TO}}/I_{\text{LO}}\) in Fig. 3a. Regions I–IV were labelled in all insets of Fig. 3.

In Fig. 3 it can be clearly seen that in region II, in addition to the linearity of \(I_{\text{TO}}/I_{\text{LO}}\) ratio along the bevel length, there is also a linearity of the dependences \(I_{\text{TO}}\) and \(I_{\text{LO}}\). We suppose that LO intensity decreases linearly in region II (Fig. 3c) due to a linear increase of the volume in which PE–PLP coupling of photoexcited electron–hole plasma with LO–phonon is present. This volume does not contribute to scattering by LO–phonon. The observed behaviour may be attributed to the following reasons:

(i) Photoexcited electrons are strongly attracted to the surface by unsaturated atomic bonds. Due to the fact that some of the surface atomic bonds are saturated by free intrinsic electrons from ionized Si-atoms, the amount of photoexcited electrons attracted to the surface will be lower in the depletion layer than in the UD GaAs layer. Hence the number of the photoexcited electrons, which are not attracted to the surface, i.e., the rest of photoexcited electrons (R-PE), is increasing. This increase is linear due to the linear increase of the volume underneath the bevel surface. It is reasonable to assume that R-PE electrons are located in the volume, which increases also linearly along the bevel. At the same time the linear increase of R-PE electrons causes a linear increase of the average intensity of the surface electric field (SEF).

(ii) Photoexcited holes are swept and confined to the surface due to the SEF. We assume that the linear increase of the average intensity of SEF causes a linear increase of the concentration of photoexcited holes in the volume underneath the surface, which also increases linearly.
From the analysis above we can conclude that R-PE electrons and photoexcited holes are located in a linearly increased volume.

The increase of the TO intensity is caused by the influence of the increased intensity of the $P_H$ mode. This mode is visible in Fig. 1a in position 3 as a broadening of the LO peak to the lower values of the Raman shift. Creation of this mode in region II can be better seen in Fig. 4a. In this figure, the difference of Raman spectra in the examined position of 4.150 mm on the bevel length (bl) and in the position on the UD GaAs is plotted. We see the modes $P_H$ and $P_E$ of the coupling of photoexcited holes and R-PE electrons with LO-phonon. Besides this feature we see a decrease of LO intensity. $P_E$ mode represents the “+” mode of the coupling of R-PE electrons with LO-phonon. Its frequency position is $294 \text{ cm}^{-1}$ and corresponds [14,15] to the concentration of electrons of about $1 \times 10^{17} \text{ cm}^{-3}$. The “–” mode which corresponds to this concentration should be positioned near 100 $\text{ cm}^{-1}$. We did not detect this mode due to its low intensity. $P_H$ mode, the mode of PE–PLP coupling of photoexcited holes was detected only alone. This is due to a strong damping effect, which results from the high effective mass of the holes. This is consistent with the previous studies [16,17] of the hole-plasma in bulk p-doped GaAs, where only one PLP mode of the coupling of holes with LO-phonon was also detected.

In Fig. 4b and c there are drawn the differences of the spectra in region II for higher values of the bevel length. We can see the broadening of the $P_H$ mode and its shifting to the lower values of the Raman shift, closer to the TO frequency position. Hence, in this way the $P_H$ mode influences the TO intensity and causes a linear increase of the TO intensity in region II (see Fig. 3b). Quantitative confirmation of this
Fig. 4. Difference of the Raman spectra in the examined position on the bevel (marked by the value of the bevel length, bl) and in the position on UD GaAs: (a) bl = 4.150 mm, (b) bl = 4.170 mm, (c) bl = 4.206 mm, (d) bl = 4.242 mm, (e) bl = 4.8 mm. Labels PE and PH denote the PE–PLP modes created by the coupling of the photoexcited electrons and holes with the LO–phonon respectively. Labels LO, TO, L_, and L_+ denote well-known LO–phonon, TO–phonon and L_, and L_+ mode of the PLP coupling, respectively.
influence is not straightforward and will be studied in our future work but we will try to solve it in future.

As far as we know [1,5,10], the study of the PE–PLP modes of the coupling between LO–phonon and photoexcited plasma in n-GaAs under CW condition at RT was not reported until now. Raman spectra influenced by photoexcited plasma in high purity GaAs were reported [7] at “helium temperature” and at laser excitation in quasi-stationary conditions. These spectra excited with 514.5 nm line of Ar laser consist of four bands. One of them (40.15 meV) could be attributed to the PH mode. Enhancement of the Raman intensity between TO–phonon and LO–phonon lines (about at 35 meV) could be caused by the influence of the PH mode. The influence of the photoexcited plasma on the Raman spectra taken along the bevelled Si-δ-doped GaAs layers was presented also in our earlier works [18,19].

Another obtained result we present is the study of the modes of PLP coupling of photoexcited electrons and holes under CW conditions at RT in the depletion layer of homogenously n-doped GaAs films. Detection of these modes was possible due to using bevelled forms of samples, which allow to examine the depletion layer alone and to study creation and evolution of these modes separately from the PLP modes of the coupling of intrinsic carriers with LO–phonon.

Now, we will continue the analysis of the dependences presented in Fig. 3. In Fig. 3b and c it is possible to see that dependences of the intensities LO and TO are linear along the bevel in region II. From this fact one can conclude that the dependence \( I_{TO}/I_{LO} \) is hyperbolic along the bevel. From Fig. 3d we see that this is true in a short limit of the depletion layer. Experimental points (EXP) are in good correlation with the calculated hyperbolic function (CALC). But in region II, the experimental dependence can be fitted well also by a linear function; differences of the fitted and experimental dependences are in the range of experimental accuracy. Linearity of the dependence \( I_{TO}/I_{LO} \) in region II was experimentally observed not only in this sample but at all structures. For quantitative physical interpretation of this phenomenon other additional experiments are needed, especially low temperature measurements at various power densities and excitation with shorter wavelengths.

The changes of the \( I_{TO} \) and \( I_{LO} \) intensities depend on the changes of the intensities of \( P_H \) and \( P_E \) modes. In Fig. 4a–c we see the evolution of these modes in region II:

(i) \( P_H \) mode is broadened and shifted to lower values of the Raman shift (from 285 to 272 cm\(^{-1}\)). This is caused by an increase of the concentration of photoexcited holes in the plasma, especially under the surface, where the highest intensity of SEF and the highest power density of laser light are present. Our assumption is supported by a similar shift of the PLP mode in the p-doped GaAs with increased concentrations of holes [16,17]. We suppose that damping of free holes in highly doped p-GaAs is different from the damping of the photoexcited holes in the depletion layer of n-doped GaAs. Therefore it is not possible to appreciate the concentration of the photoexcited holes from the position of \( P_H \) mode using the results obtained in [17].

(ii) \( P_E \) mode is slightly broadened and shifted from 294 to 297 cm\(^{-1}\) due to the increase of concentration of photoexcited electrons coupled with LO–phonon. In the depletion layer saturation of the surface bonds by intrinsic electrons increases, therefore more photoexcited R-PE electrons create the photoplasma. Its concentration is about \( 10^{17} \) cm\(^{-3}\), as we can derive [14,15] from the shift of \( P_E \) mode. The \( P_E \) mode represents the concentration of the R-PE electrons rather than the concentration of all photoexcited electrons. Therefore the concentration of photoexcited electrons derived from the frequency position of \( P_E \) mode will be lower than the concentration of photoexcited holes derived from \( P_H \) mode.

Now we will discuss the behaviour of the photoexcited plasma in regions III and IV. In Fig. 4d, which represents region III in addition to scattering in the depletion layer the scattering in SCR will be present. We note that in Fig. 4 are the dependencies of differences of Raman spectra in the examined position and spectrum obtained from the position on UD GaAs layer, therefore we do not consider the scattering in UD GaAs layer. The SCR is characterized by a steep concentration profile of free intrinsic electrons. The
average concentration of the electrons in SCR is lower than in GaAs:Si-doped layer. Scattering in SCR is represented by PLP modes L+ and L− arising from the coupling of free electrons in the SCR with LO-phonon. The L− mode is close to TO peak (268 cm−1) and L+ is positioned at 550 cm−1. This value corresponds to the concentration of free electrons 2.2 × 10^{18} cm−3. In the same figure we see P_H and P_E modes of the PE–PLP coupling. The P_E mode is slightly broadened and its maximum is shifted to 300 cm−1. This is caused by the increase of the concentration of R-PE electrons, which is different than in region II. The electric field created in SCR is opposite to the SEF, therefore, the distribution of photoexcited electrons will be changed. The PH mode opposite to the SEF, therefore, the distribution of

\begin{equation}
\frac{I_{TO}}{I_{LO}} = \frac{N}{2.16 \times 10^{18} \text{cm}^{-3}}
\end{equation}

At such high doping level the error is about 10%. For concentrations 1 × 10^{17} cm−3 the dependence is considerably changed. The value of Der \((I_{TO}/I_{LO})\) achieves a significantly lower value than predicted by
the fitting function (1) and the error in the estimation of this value increases to about 20–30%. The precise nature of the dependence in this low concentration region can be estimated by performing measurements on more samples with doping concentrations below the value $5 \times 10^{17}$ cm$^{-3}$.

The dependence in Fig. 6 together with formula (1) provides an effective tool to determine the doping concentration of Si-doped GaAs layers. Due to a large magnification of vertical structure we are able to determine the doping level also in very thin layers (nanometer range), where it is not possible to use other well-known methods, e.g., Van der Pauw and Hall measurements, PLP modes of Raman spectroscopy, and C–V method. Formula (1) was used to determine the doping level in 30-nm thin Si-doped GaAs layers. The results were compared with secondary ion mass spectroscopy (SIMS) measurements and very good correlation was obtained [20]. The presented method is a useful tool also for determining the concentration profile in non-homogeneously doped very thin layers. We used formula (1) as a calibration function to determine the doping concentration in Si–δ-doped GaAs layers [21]. Good agreement of our values with those obtained by SIMS method was achieved.

4. Conclusion

We have studied the properties of the photoexcited plasma in n-doped GaAs and its influence on micro-Raman spectra. The spectra were recorded in different positions of the laser spot along the bevelled structure. In the surface depletion layer, we have detected the modes of the coupling of photoexcited free carriers with LO–phonon by CW condition at room temperature. The modes $P_H$ and $P_E$ of this coupling were positioned in the range of the Raman shift $285–272$ cm$^{-1}$ for photoexcited holes and $294–300$ cm$^{-1}$ for photoexcited electrons, respectively. We observed significant changes in the intensities of TO–phonon and LO–phonon modes along the bevel. In the surface depletion layer the dependence of the ratio of the intensities of TO–phonons and LO–phonons, $I_T/\omega_{LO}$
was linear along the bevel length. The first derivative of this dependence is a characteristic value, which corresponds to the doping concentration. We determined these values in all measured structures doped by Si with different doping levels. The obtained dependences and fitted formula are the effective tool to determine the doping profile in the very thin layers, where other known method cannot be used or their results are handicapped by high errors.

Acknowledgements

This work was supported by the NATO grant PST.CLG. 978729, by the DAAD PPP grant 9/2003, by the VEGA grants 1/0152/03, 1/0154/03, 1/9042/02, by the Wroclaw University of Technology statutory grant and by Project of Poland/Slovakia cooperation.

References