LASER RAMAN SPECTROSCOPY STUDIES OF FREE CARRIERS' INTERACTION WITH OPTICAL PHONONS AND SURFACE SPACE CHARGE EFFECT ON PHONON SPECTRUM IN GAP

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Accepted for publication April, 2006

ABSTRACT. In the present work free carriers' interaction with phonons both with volume and surface excitation has been investigated. Having studied the regularity of plasmon-phonon interaction in GaP, effect of electric field, induced by surface space charge, on phonon spectrum has been revealed. At volume excitation LO phonon's halfwidth is being widen in GaP according to a certain rule as a result of increase of free carriers and the mentioned widening is far distinctly expressed in *p*-GaP. After surface excitation it was found that on shortening of wavelength of exciting laser LO phonon halfwidth sharply decreases with increase of free carrier's concentration. Such an effect was fixed from (001) surface of GaP. In the process of investigation of (110) surface it has been found that at small concentration of electrons forbidden LO phonon is still observed from (110) surface with sufficient intensity. With increase of electron concentration LO phonon intensity increases pronouncedly and its intensity prevails over intensity of TO phonon. After covering surface (110) of GaP with semitransparent metal film of aluminum intensity of LO phonon increases still more. The observed experimental results we have explained in terms of formation of electron depletion surface layer due to electric field induced by space charge.

When impurities in GaP are in abundance to form free carriers, then interaction between longitudinal optical LO phonons and electric field generated by charge density fluctuation of free carriers takes place. As a result of this interaction a bound state of two elemental excited particles, LO phonon and plasmon, is formed.

Free carriers in semiconductors display plasma properties with characteristic plasma frequency:

$$\varpi_p = \left(\frac{4\pi Ne^2}{\varepsilon_\infty m^*} \right)^{1/2} \quad (1)$$

Where N is charge carriers' concentration, e-electron charge, ε_∞ - dielectric permittivity of high-frequency and m^* - charge carriers' effective mass. Plasma vibration is a longitudinal wave of charge density. Perturbation caused by this wave, forms electric field interacting with electric field of polar vibrations of crystal lattice in polar semiconductors. Thus, as a result of interaction of longitudinal optical mode LO with plasma vibration, the bound plasmon-phonon vibrations are produced (which include common ion and electron motions) with a new, different frequency.

If damping of plasma vibration is ignored, the solution of equation for plasmon-phonon modes' frequencies will be as follows:

$$(\omega_\pm^0)^2 = 1/2(\omega_{LO}^2 + \varpi_p^2) \pm ½[(\omega_{LO}^2 + \varpi_p^2)^2 - 4\omega_{TO}^2\varpi_p^2]^{1/2} \quad (2)$$

Experimentally observed plasmon frequencies ω_+ and ω_- ($\omega_+ > \omega_{LO}$, $\omega_- < \omega_{TO}$) are in good agreement with theoretical expression (2).

When studying plasmons and polar phonons interaction both conductivity type (n or p) and energy-band structure should be taken into consideration.

On recording and study of characteristic spectrum of plasmon-phonon interaction of other semicoductors of A^3B^5 type, for instance, GaAs, the spectrum shows frequency peaks of LO and TO phonons and simultaneously frequency peaks, v_+ and v_-, respectively, of plasmon-phonon interaction of high and low frequency branches, four peaks altogether.

Plasmon-phonon mode frequency v_+ is closely approximated to LO phonon frequency, v_{LO}, over the range of possible doping by impurities of GaP ($\sim 10^{16} \div 10^{19}$ electron cm^{-3}). In such a case only

three peaks of ν_-, ν_{TO}, ν_+ are seen in Raman scattering spectrum. With doping order increase (free carriers' number increases) plasmon-phonon peaks' frequencies are displaced towards high frequencies and broadened. For finite value $\nu_p \to 0$ (undoped gallium phosphide), $\nu_+ \to \nu_{LO}$ and spectral band half-width of high frequency branch of plasmon-phonon mode approximates to the half-width of optical phonon band, $\Gamma_+ \to \Gamma_{LO}$. Spectral bands corresponding to low frequency branch has not been detected yet in GaP, probably, because of their too low intensity or due to other physical difficulties.

Plasmon-phonon interaction in GaP has been studied in some papers [1-4]. In all of these papers free carriers interaction with polar phonons has been studied by 632.8 nm wavelength excitation of helium-neon laser. This is equivalent to volume excitation of GaP, when surface and resonant effects do not affect plasmon-phonon interaction.

The purpose of the present paper is to study plasmon-phonon interaction in *n*- and *p*-type GaP by 632.8 nm volume excitation as well as plasmon-phonon interaction from near-to-surface layers. Toward this end besides 632.8 nm wavelength of helium-neon laser the following wavelengths of argon, krypton and helium-cadmium lasers nave been used to excite Raman spectra: 568.2; 514.5; 488.0; 476.5; 457.9; 441.6 nm. The spectra had been analyzed on lab-type laser Raman spectrometer constructed on basis of double monochromator DFS-24 described in [5].

Gallium-phosphide with electron conduction as well as with hole conduction has been studied. At the same time Raman spectra of high-resistance semi-insulating GaP have been recorded too. One category of *n*-GaP monocrystals was doped with sulphur, electron concentration being $2 \cdot 10^{17}$ cm^{-3}, the second one was doped with tellurium, electron concentration being $2.2 \cdot 10^{18}$ cm^{-3}, the third category of monocrystals was undoped specially, it was of *n*-type with electron concentration in it not exceeding 10^{16} cm^{-3}. A monocrystal of *p*-GaP was doped with Zn, the hole concentration being $5 \cdot 10^{18}$ cm^{-3}. A compensated monocrystal of GaP, semiinsulating, with conductivity 10^{12}-10^{14} ohmxcm and electron concentration not exceeding 10^{14}cm^{-3} has been also studied. The monocrystal's surfaces were of (001) and

(111) orientations. All the measurements were made at room temperature.

As is well known, GaP is an indirect band gap semiconductor with zinc blend structure. The value of its minimum indirect band gap is 2.26 eV and that of the first direct band gap is 2.79 eV at room temperature. Accordingly the skin-layer corresponding to the abovementioned exciting wavelengths has different values. Therefore, for wavelengths 632.8 and 568.2 nm GaP is transparent and volume excitation takes place. Through other wavelengths surface layers' (having different thicknesses) monitoring takes place. Besides, for the shortest waves resonance Raman scattering (RRS) takes place as we have shown in [6].

Fig.1 shows Raman spectra of GaP for two different quantities of free carriers. The first crystal is compensated with chromium, semi-insulating, with electron concentration not exceeding 10^{14} cm^{-3}. The second is of hole conduction, doped with zinc impurities, with hole concentration equal to $6.9 \cdot 10^{18}$ cm^{-3}. In both cases Raman scattering spectra were excited by helium-neon gaseous laser emission λ_L = 632.8 nm. Such an experimental situation enables one to carry out analysis of scattered light from the whole volume rather than from small surface skin-layer.

The spectra in Fig.1 show clearly that in *p*-type semiconductor with the hole concentration increase, spectral band halfwidth characterizing LO optical phonon increases distinctly becoming Γ_+ = 10.5 cm^{-1}. At the same time this peak is shifted towards high frequencies for about $3cm^{-1}$ (Fig.1b) from LO optical phonon (characterizing a high-resistance crystal) peak frequency at 402 cm^{-1} (Fig.1a). The mentioned peak is identified, as mentioned in theoretical part of the paper, as plasmon-phonon interaction peak of high-frequency branch. In this case free heavy holes produce plasmon vibrations.

Raman scattering spectra of *n*-GaP doped with donor-type impurities, sulfur in the first case and tellurium in the second, recorded for λ_L = 488.0 nm (2.54 eV) excitation of ion laser emission have been studied. The electron concentration was $2 \cdot 10^{17}$ cm^{-3} in *S*-doped samples and $2.2 \cdot 10^{18}$ cm^{-3} in Te-doped ones. For the purpose of comparison the spectrum of semi-insulating GaP has been also

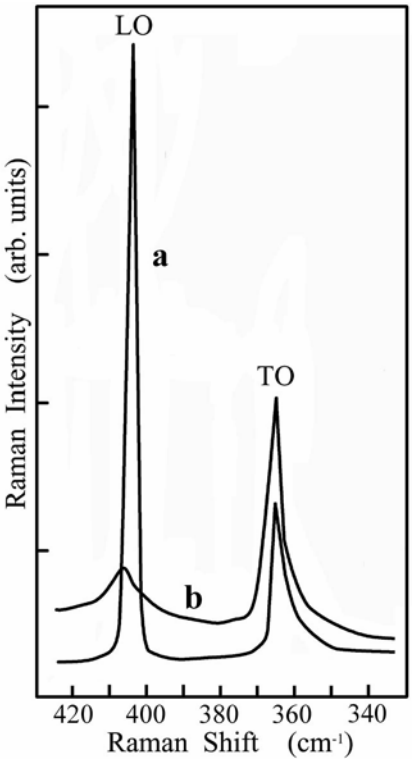

Fig.1. Raman spectra of high-resistance GaP (1a) and GaP with $6.9 \cdot 10^{18}$ cm^{-3} concentration of holes (1b); excitation 632.8 nm.

recorded with electron concentration not exceeding 10^{14} cm^{-3}. The spectra show LO phonon halfwidth increase with electron concentration increase. Peak displacement also takes place though by far less amount than in case of Zn-doping. Peak broadening also is far less than in case of Zn-doping. In this case Raman scattering cannot be considered as volume excitation. The skin-layer is about 15 mmk and therefore it is more reasonable to speak of scattering characterizing near-to-surface layer. Besides, as shown in [6], at excitation with the energy mentioned above, RRS, occurring with direct band gap mechanism, is started. Raman spectra for the same samples have been recorded also in conditions of volume excitation with 632.8 nm

(1.98 eV) and 568.2 nm (2.18 eV) wavelengths. In all three cases plasmon-phonon interaction picture (small shift of LO phonon's peak frequency and halfwidth's broadening) is invariable; LO phonon halfwidth for semi-insulating GaP is 1.8 cm^{-1}, whereas for *n*-GaP with electron concentration $2.2 \cdot 10^{18}$ cm^{-3} halfwidth is 3.8 cm^{-1}.

Fig.2 shows Raman spectra of *p*-GaP excited by krypton laser wavelength λ_L =568.2 nm (2.18 eV), argon laser emission λ_L = 457.9 nm (2.708 eV) and helium-cadmium laser wavelength λ_L = 441.6 nm (2.808 eV). Spectra excited with other wavelengths are not shown in the above figure.

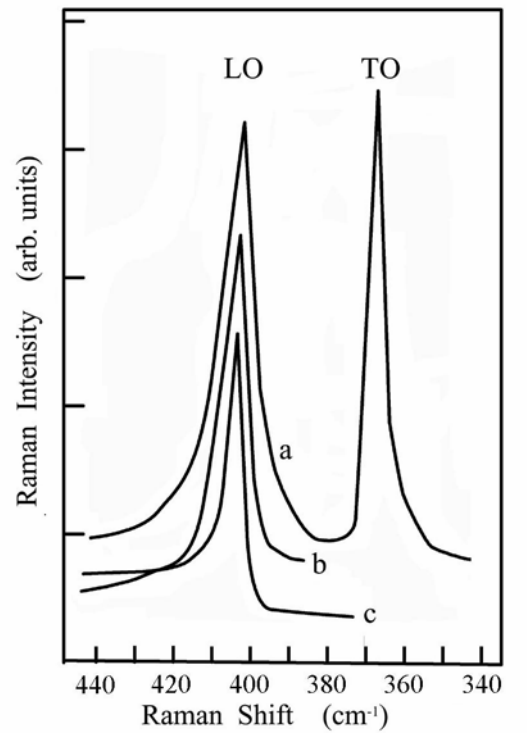

Fig.2. Raman spectra of Zn-doped ($p=6.9 \cdot 10^{18}$ cm^{-3}) GaP; excitation: a-568.2, b-457.9, c-441.6 nm.

The aforecited experimental spectra show that the halfwidth of plasmon-phonon interaction peak of high frequency positive branch has narrowed by shortening of exciting laser wavelength, i.e. by high energy laser quanta excitation. We were the first to reveal the mentioned effect in GaP [7].

Fig.3 shows a graph plotted on the ground of the above experimental data. It shows clearly the effect we, the first, have revealed in GaP, namely, sharp decrease of halfwidth of LO phonon permitted by Raman scattering selection rule proportionally to exciting laser wavelength shortening. This effect is expressed especially distinctly in *p*-GaP being enhanced near the first forbidden band E_1 at RRS. We think the mentioned effect to be bound up with electron depletion layer formed by surface electric field induced by surface space electric charge. To prove the consideration, peculiarities of electric field induced Raman scattering (EFIRS) in GaP have been studied. It should be noted that surface electric fields' effect on Raman scattering has been widely studied almost for all semiconductors of A^3B^5 type, especially for GaAs. Exception is only GaP; the reason of it lies in surface peculiarities of GaP.

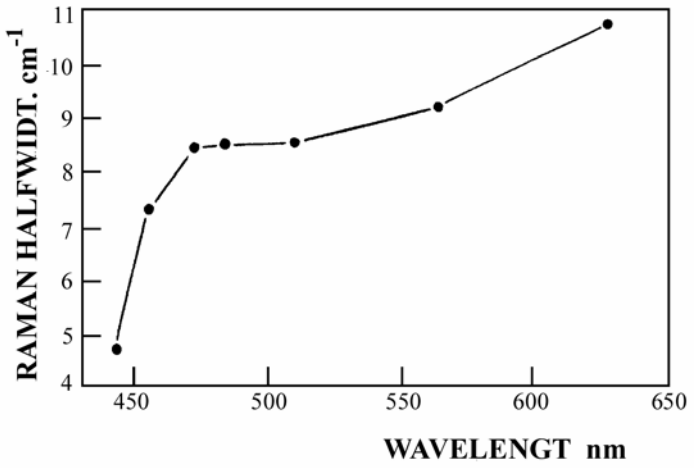

Fig.3. Dependence of LO phonon halfwidth upon exciting laser wavelengths.

Generally at a semiconductor crystal surface always exists internal electric field, which is the result of space charge layer at the surface. One can consider charge carrier depletion layer in the frame of Schottky barrier model. In this approximation interrelation between surface electric field E_s, Schottky barrier's height Φ_B and concentration of current curriers N is determined by the formula

$$E_S = 2 \cdot \left(\frac{2\pi \cdot \Phi_B \cdot N}{\varepsilon} \right)^{1/2}, \tag{3}$$

where ε is static dielectric susceptibility of semiconductor. In contrast to a dielectric, when it is placed in external electric field, the electric field in semiconductor depletion layer is not constant through the overall width Z_d of depletion layer, which is expressed as

$$Z_d = \left(\frac{\varepsilon \cdot \Phi_B}{2\varepsilon \, \mathrm{e}^2 \cdot N} \right)^{1/2}, \tag{4}$$

and the surface charge is

$$Q_{SC} = \frac{\varepsilon \cdot E_S}{4\pi}. \tag{5}$$

Potentials and electric fields in depletion layer in case of fixed barrier height Φ_B and two different concentration carriers N has been computed for GaAs. The electric field turned to be maximum at surface and falls linearly in the depletion layer width Z_d. Hence, EFIRS study is actually for opaque semiconductors, i.e. when light penetration depth in semiconductor is less than or approximately equal to depletion layer thickness.

In the next experiment we used monocrystal of *n*-GaP with (110) orientation and two different electron concentrations 10^{16} and $5 \cdot 10^{17}$; we used 441.6 nm wavelength to excite Raman-spectra and recorded Raman-spectra of these semiconductors at room temperature (Fig.4).

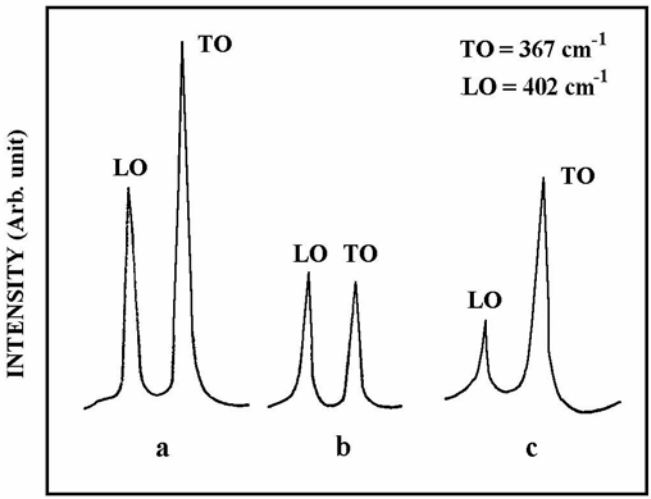

Fig.4. Raman spectrum from (110) surface of GaP at 441.6 nm excitation: a – n = 10^{16} cm^{-3}; b - $5 \cdot 10^{17}$ cm^{-3}; c - $4 \cdot 10^{18}$ cm^{-3}

It is seen from the spectra that the forbidden LO phonon is of weak intensity at low concentration of electrons in semiconductor (10^{16}) and is far less in comparison with TO phonon (Fig.4a). When electron concentration increases in semiconductor (sample with electron concentration $5 \cdot 10^{17}$), its Raman-spectrum shows clearly that the forbidden LO phonon intensity increases sharply (Fig.4b).

Thus, in resonance conditions, when exciting (110) electron-doped surface of GaP, LO phonon forbidden by law of symmetry is observed in Raman spectrum and its intensity increases with electron concentration increase.

Quite different picture is observed when recording Raman-spectra of a *p*-type GaP at 441.6 nm excitation. In this case, when hole concentration is $4 \cdot 10^{18}$ cm^{-3}, the forbidden LO phonon intensity in Raman-spectra recorded from (110) surface is far weaker, than in case of *n*-type GaP, when electron concentration is 10^{16} cm^{-3}. That is shown in Fig.4c.

Raman-spectra of metallized (110) surface look very interesting. First we recorded RS-spectrum from that part of surface, which was not covered with metal and served as a standard. Recording was made in resonance condition. The forbidden LO phonon at 402cm^{-1} and permitted TO phonon at 367cm^{-1} appeared in Raman-spectra with ratio of intensities just registered in abovementioned experiments, when concentration of electrons in bulk crystal was 10^{16}cm^{-3} (Fig.5a). Then Raman-spectra from the second, metallized part of the (110) surface clearly showed even greater increase of the forbidden LO phonon intensity (Fig.5b).

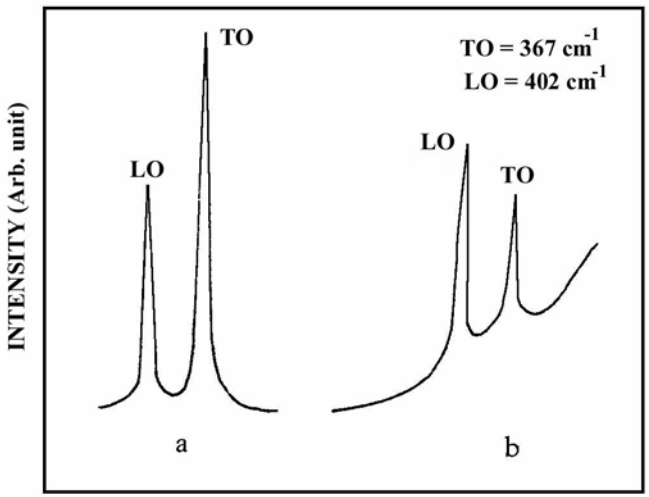

Fig.5. Raman spectrum from (110) surface of GaP at 441.6 nm excitation and free carrier concentration 10^{16} cm^{-3}: a-without aluminum covering; b-with aluminum covering

Thus the experiments we first have carried out for GaP to study surface field effect on the mentioned crystal Raman-spectra, give experimental results as follows: Raman-spectra from (110) surface of *n*-type GaP hardly show the forbidden LO phonon when electron concentration is equal to 10^{16}cm^{-3}; the intensity of the forbidden phonon increases sharply when electron concentration in bulk crystal increases and becomes $5\cdot10^{17}$cm^{-3}; This intensity increases more when

we cover this surface with semitransparent aluminum layer; in case of a *p*-type GaP when hole concentration is $4 \cdot 10^{18}$, the intensity of forbidden LO phonon is very small. In all cases the intensity of TO phonon permitted by selection rules is constant; the mentioned effects become apparent clearly only at resonance Raman scattering.

In doped semiconductors the concentration of current carriers at surface generally differs sharply from a bulk concentration, which is caused by existence of surface space charge layers. The structure of these layers is determined by the Fermy level state at surface, while the Fermy level itself depends upon density and character of surface states. In that way, the natural layer of space charge expresses properties of surface. For example, in case of surface of GaAs polished in air, Fermi level is pinned in the middle of forbidden gap. Because of this the surface of GaAs both *n*-type and *p*-type is depleted. At the same time it is proved that there are no eigen surface states on (110) surface of very pure GaAs, polished or cleaved in high vacuum, which will be arranged in bulk forbidden gap. Band bending is not formed on such surfaces and accordingly there is no pinning of Fermi level at all.

Among A^3B^5 group semiconductors GaP is the only one, surface levels of which may be exist in conditions of high vacuum. Therefore it is rather difficult to interpret EFIRS theoretically for the mentioned semiconductor, but it is necessary to accumulate certain experimental data.

Skin-layer is about 500 nm for 441.6 nm wavelength in GaP. Schottky barrier width in A^3B^5 semiconductors changes from about 2000Å to 150Å when current carriers concentration changes from 10^{16} to $5 \cdot 10^{18}$ accordingly. So, during all of our experiments light penetration distance is much more than depletion layer thickness. The fact has not been found in any EFIRS experiments yet. Our measurements for indirect gap GaP were made in resonance conditions at direct E_1 gap. In such conditions absorption factor α at 441.6 nm is 2000 cm^{-1} and skin-layer accordingly is large. I.e. in fact we are registering resonance Raman-spectra from two layers, one of which is wide, about 500 nm, but LO phonon is forbidden from this layer and there will be no signal. As to the second layer, the width of which is defined from (4) and is various according to carrier

concentration but not exceeds a few hundred Angstroems, resonance Raman-spectra are constantly registering forbidden LO phonons of great intensity. Therefore, on the base of abovementioned experimental facts we connect this phonon induction mainly with surface electric field. Sharp increase of forbidden LO phonon intensity from GaP (110) surface covered with aluminum layer speaks in favor of this mechanism.

So, in conditions of Resonance Raman scattering the peculiarities of plasmon-phonon interaction have been studied in GaP. Absolutely new two experimental facts have been fixed for GaP after studying free carriers' influence on GaP phonon spectrum with surface excitation, especially in conditions of resonance Raman scattering: a) above mentioned is manifestation of allowed LO phonon of Raman scattering, non-interacting with free carriers from depletion layer of (001) surface of *p*-GaP; b) discovering of forbidden LO phonon of Raman scattering in resonance conditions from (110) surface of *n*-GaP induced by surface electric field of surface space charge.

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დენის თავისუფალი მატარებლების ოპტიკურ ფონონებთან ურთიერთმოქმედებისა და ზედაპირული სივრცითი მუხტის ფონონურ სპექტრზე ზეგავლენის შესწავლა GaP-ში ლაზერული რამან სპექტროსკოპიით

დასკვნა

პლაზმონ-ფონონური ურთიერთმოქმედება A^3B^5 ტიპის ნახევარგამტარებში ფართოდაა შესწავლილი. რამოდენიმე შრომაში ეს მოვლენა შესწავლილია GaP-შიც, მაგრამ მხოლოდ მოცულობითი აღგზნებით. პლაზმონ-ფონონური ურთიერთმოქმედება GaP-ში შევისწავლეთ ზედაპირული აღგზნებით, თანაც - რეზონანსულ პირობებში. აღმოვაჩინეთ, რომ პლაზმონ LO - ფონონის ურთიერთმოქმედების მახასიათებელი სპექტრალური ზოლის ნახევარსიგანე, რომელიც მოცულობითი აღგზნებისას ფართოვდება დენის თავისუფალი მატარებლების კონცენტრაციის ზრდით, ანომალურად დავიწროვდა აღმგზნები ლაზერის ტალღის სიგრძის დამოკლებისას. ეს ეფექტი, რომელიც უფრო გამოხატული გახდა რეზონანსული რამანის გაბნევისას E_1 ზონის მახლობლობაში, ჩვენ პირველებმა დავაფიქსირეთ GaP-ში (001) ზედაპირიდან.

ჩვენი მოსაზრებების დასადასტურებლად შევისწავლეთ რამანის გაბნევა (110) ზედაპირიდანაც. ამ შემთხვევაშიც პირველებმა აღმოვაჩინეთ, რომ GaP-ს (110) ზედაპირიდან შერჩევის კანონით აკრძალული LO ფონონის ინტენსიობა მკვეთრად გაიზარდა მოცულობითი დენის თავისუფალი მატარებლების ზრდისას. ეს ეფექტი განსაკუთრებით გაძლიერდა რეზონანსული რამანის გაბნევისას და კიდევ უფრო გაძლიერდა, როდესაც (110) ზედაპირზე დავაფინეთ ნახევრადგამჭვირვალე ალუმინის მეტალის ფენა.

ორივე ახლად აღმოჩენილი ექსპერიმენტული ფაქტი ადასტურებს ჩვენს მოსაზრებას, რომ მოვლენა უნდა აიხსნას რამანის გაბნევაზე GaP-ს ზედაპირთან სივრცითი

მუხტის ფენით ინდუცირებული ზედაპირული ელექტრული ველის ზეგავლენით. შედეგად, ზედაპირის გარკვეულ სიღრმეზე წარმოიქმნება დენის თავისუფალი მატარებლებით გაღარიბებული ფენა, რაც ბუნებრივია, იწვევს ამ ფენიდან მხოლოდ სუფთა ფონონური ზოლის დამზერას, რომელიც არაა გაფართოებული პლაზმონურ რხევებთან ურთიერთმოქმედებით.