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THE EFFECT OF IMPURITIES ON ACOUSTIC PROPERTIES OF GALLIUM PHOSPHIDE

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This paper presents results of measurements of propagation velocity and attenuation coefficient of an acoustic wave, and phonon-phonon coupling constant in pure GaP crystals and with impurities. Measurements were carried out with the utilization of Bragg type diffraction of laser light on an acoustic wave in frequency range from 0.2 to 1.5 GHz.

The elastic constants versus impurity concentration dependence was determined from measurements of propagation velocity of an acoustic wave. It was found that the c_{11} constant changes most of all, while the c_{12} and c_{44} change less. c_{11} and c_{44} constants decrease with the increase of impurity concentration and the c_{12} constant increases slightly. Assuming, that intervalley electron transitions are the main cause for changes of the elastic constants the deformation potential constant was calculated.

From investigations of the relationship between the attenuation coefficient and impurity concentration it was stated that attenuation in crystals with impurities exceeds attenuation in pure crystals and that the difference increases with frequency. The relaxation time, which is characteristic for intervalley electron transitions, was determined on the basis of measurements of the attenuation coefficient.

The influence of impurities on the phonon-phonon coupling constant was not stated.

W pracy przedstawiono wyniki pomiarów prędkości propagacji i współczynników tłumienia fali akustycznej oraz stałych sprzężenia fonon-fonon w czystych i domieszkowanych kryształach GaP. Pomiary przeprowadzono wykorzystując dyfrakcję Bragga światła laserowego na fali akustycznej w przedziale częstotliwości od 0.2 do 1.5 GHz.

Z pomiarów prędkości propagacji fali akustycznej wyznaczono zależność stałych sprężystych od koncentracji domieszek. Stwierdzono, że najbardziej zmienia się stała c_{11}, w mniejszym stopniu stała c_{12} i c_{44}. Stałe c_{11} i c_{44} maleją ze wzrostem koncentracji domieszek, a stała c_{12} nieznacznie wzrasta. Zakładając, że główną przyczyną zmian stałych sprężystych są międzydolinowe przejścia elektronów, wyliczono stałą potencjału deformacyjnego.

Badając zależność współczynnika tłumienia od koncentracji domieszek stwierdzono, że w kryształach domieszkowanych tłumienie jest większe niż w kryształach czystych, przy czym różnica ta wzrasta ze wzrostem częstotliwości. Pomiary współczynnika tłumienia pozwoliły wyznaczyć czas relaksacji charakteryzujący międzydolinowe przejścia elektronów.

Nie stwierdzono eksperymentalnie wpływu domieszek na stałe sprzężenia fonon-fonon.

1. Introduction

Research was aimed at the determination of the effect of impurities an acoustic properties of semiconductors. Pure and with impurities crystals of gallium phosphide GaP with three concentrations of sulfur impurities: $7.7 \cdot 10^{22}$ m^{-3}, $6.5 \cdot 10^{23}$ m^{-3} and $1.9 \cdot 10^{24}$ m^{-3}, were chosen. Crystals were obtained from the Institute of Technology of Electronic Materials in Warsaw, where also impurity concentration, carrier mobility and electric resistance of samples were determined.

At room temperature, at which measurements were performed, all impurities are ionized and investigated crystals are *n*-type semiconductors.

Lattice impurities, as well as free carriers cause changes of elastic constants of the second and third order. This, in turn, causes a change of propagation velocity and acoustic wave attenuation coefficient. Also values of phonon-phonon coupling constants change.

Within the framework of this work values of mentioned material constants were measured.

Gallium phosphide crystallizes in the cubic system, point group 43 m. Due to a relatively high value of the energy gap 2.20 eV, these crystals can be investigated with acoustooptic methods with the utilization of laser light in the visible range.

2. Experimental system

Measurements were performed with the utilization of Bragg type diffraction of laser light on a volume acoustic wave. The diagram of the set-up for measurements in shown in Fig. 1.

Investigated GaP crystals were rectangular prisms with dimensions $5 \times 5 \times 20$

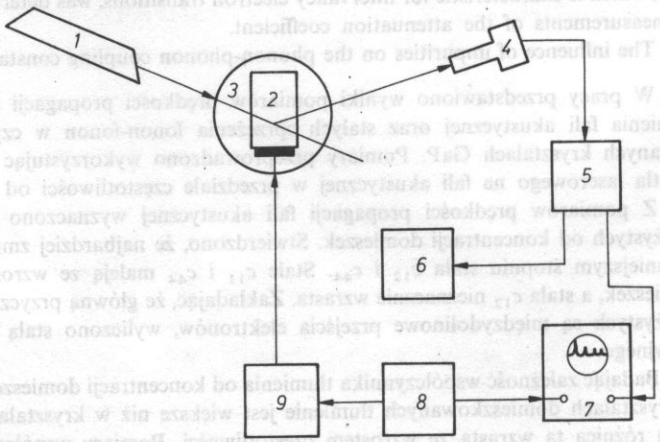

Fig.1. Diagram of measuring system *1* – laser, *2* – investigated crystal, *3* – goniometric table, *4* – multiplier phototube, *5* – selective amplifier, *6* – recorder, *7* – oscilloscope, *8* – modulating generator, *9* – high-frequency generator

mm. The parallelism of frontal planes was not worse than 5″, while the orientation accuracy was equal about 30′. Longitudinal and transverse acoustic waves were generated with $LiNbO_3$ transducers with 36° Y and X cutting, respectively. Transducers with fundamental frequency of 150–200 MHz were connected with tested crystals with an indium layer or due to adhesion. Surfacest of transducers were equal to from 2 to 5 mm^2 depending on applied frequency. High-frequency generators had the electric power of 1 W.

The propagation velocity of an acoustic wave was determined from measurements of the acoustic pulse transition time in the investigated crystal, as well as from measurements of the Bragg angle. Accuracy of velocity measurements amounted to about 0.2%.

The acoustic wave attenuation coefficient was determined with the utilization of interference of a series of waves reflected from frontal planes of the crystal at a small frequency change of these waves. This method is described in detail in paper [1]. Measurements were made in frequency range 0.2–1.5 GHz. The measurement accuracy of the attenuation coefficient equals about 10%.

Phonon-phonon coupling constants were determined from intensity measurements of light diffracted on harmonics of acoustic wave.

3. Results of measurement

Results of measurements of acoustic wave's propagation velocity in pure and with impurities GaP crystals are presented in Table 1. Values of c_{ij} constants were

Table 1. Propagation velocity of a longitudinal and transverse acoustic wave in GaP ($T = 293$ K, $f = 500$ MHz)

Impurity concentration	Direction of propagation polarization	Velocity ms^{-1}
pure	[100], [100]	5864
	[100], [001]	4156
	[110], [110]	6480
	[111], [111]	6675
$7.7 \cdot 10^{22}$	[100], [100]	5858
	[100], [001]	4150
	[110], [110]	6475
	[111], [111]	6670
$6.5 \cdot 10^{23}$	[100], [100]	5862
	[100], [001]	5150
	[110], [110]	6475
	[111], [111]	6670
$1.9 \cdot 10^{24}$	[100], [100]	5835
	[100], [001]	4145
	[110], [110]	6468
	[111], [111]	6665

determined (Table 2). On the basis of known relationships between acoustic wave's propagation velocity and elastic constants:

$$V_{[100],[100]} = \sqrt{\frac{c_{11}}{\varrho}},$$

$$V_{[110],[110]} = \sqrt{\frac{c_{11}+c_{12}+2c_{44}}{2\varrho}}, \tag{1}$$

$$V_{[111],[111]} = \sqrt{\frac{c_{11}+2c_{12}+4c_{44}}{3\varrho}},$$

$$V_{[100],[001]} = \sqrt{\frac{c_{44}}{\varrho}}.$$

Table 2. Values of elastic constants of GaP

Impurity concentration m^{-3}	c_{11} 10^{10} Nm^{-2}	c_{12} 10^{10} Nm^{-2}	c_{44} 10^{10} Nm^{-2}
pure	14.195	6.231	7.132
$7.7 \cdot 10^{20}$	14.190	6.252	7.110
$6.5 \cdot 10^{23}$	14.140	6.260	7.110
$1.9 \cdot 10^{24}$	14.058	6.280	7.094

And then angular distributions of velocities can be determined with the help of elastic constants. Figure 2 presents an exemplary velocity distribution of an acoustic wave in the XY plane in pure GaP. This distribution was calculated on the basis of determined elastic constants, and theoretical relationships between wave's velocity of propagation in an arbitrary direction and elastic constants.

Preformed measurements prove that the acoustic wave's propagation velocity is smaller in crystals with impurities than in pure crystals. Greatest differences were observed for a longitudinal wave in direction [100]. Whereas, in the case of a transverse wave in direction [100] and longitudinal waves in directions [110] and [111] much smaller differences were observed. This means that impurities cause the c_{11} constant to change the most, while elastic constant c_{44} and combination of constants $c_{11}+2c_{12}+4c_{44}$ change insignificantly. Table 3 presents changes of elastic constants: c_{11}, c_{12}, c_{44}; calculated on the basis of velocity measurements of an acoustic wave.

Performed calculations prove that the c_{11} elastic constant changes the most and the value of this constant decreases with an impurity concentration increase. The value of the c_{44} constant decreases much less while the c_{12} constant is slightly greater in crystals with impurities.

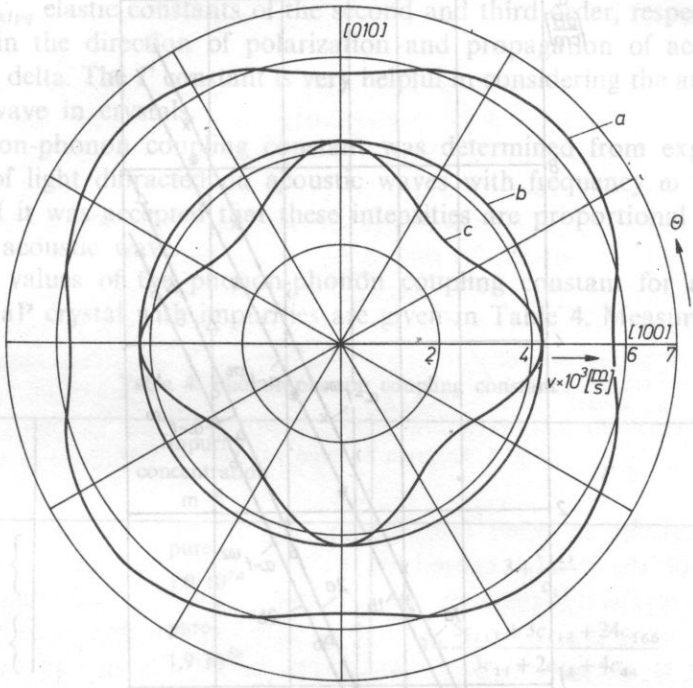

Fig. 2. Angular characteristic of propagation velocity of a longitudinal wave a and transverse waves b, c in the XY-plane in a pure GaP crystal

Table 3. Changes of elastic constants of GaP ($\Delta c_{ij} = c_{ij}(0) - c_{ij}(n)$)

Impurity concentrations m^{-3}	Δc_{11} 10^{10} Nm^{-2}	Δc_{12} 10^{10} Nm^{-2}	Δc_{44} 10^{10} Nm^{-2}
$7.7 \cdot 10^{22}$	0.005	−0.021	0.022
$6.5 \cdot 10^{23}$	0.055	−0.029	0.022
$1.9 \cdot 10^{24}$	0.132	−0.049	0.038

Figure 3 shows results of measurements of the attenuation coefficient for a longitudinal and transverse acoustic wave in direction [100] in a pure crystal and crystal with 1.9×10^{24} m^{-3} impurity concentration. Next to approximating lines — determined with the method of least squares — relationships between the attenuation coefficient and frequency are given. Measurements prove that the acoustic wave effect of damping is greater in crystals with impurities than in pure crystals, and the difference incereases with a frequency increase.

Also the phonon-phonon coupling constant was determined for two crystallographic directions with the application of Bragg type diffraction of laser light on an acoustic wave.

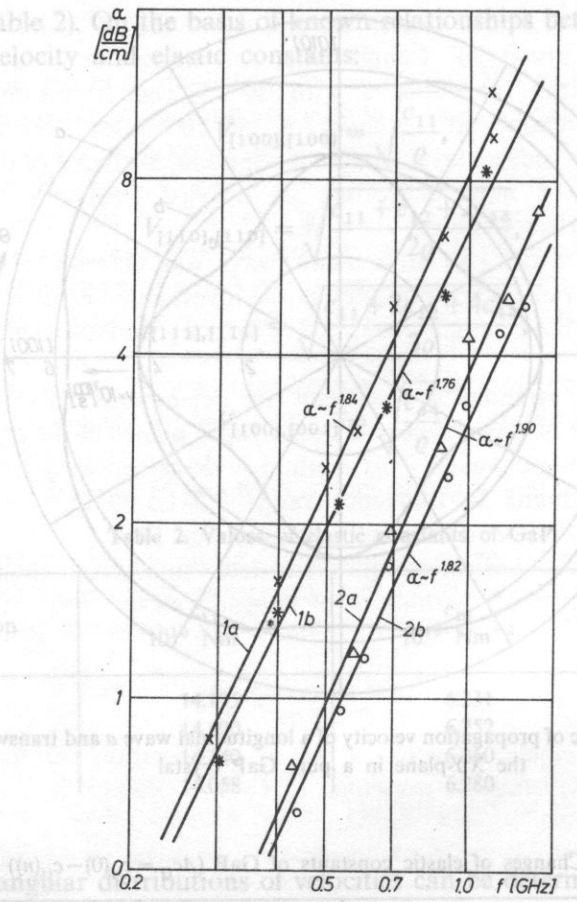

Fig. 3. Wave attenuation coefficient versus frequency, direction of propagation – [100], *1* – longitudinal wave, *2* – transverse wave with polarization [001] *a* – pure crystal, *b* – crystal with impurity concentration $\cdot 1.9 \cdot 10^{24}$ m^{-3}

If an acoustic wave with frequency propagates in a crystal, then a wave with frequency 2ω is generated due to the anharmonicity of interatomic forces. The intensity of this wave is expressed by [2]:

$$I_2(x) = \frac{\Gamma^2 q^2 I_1^2(0)}{8\varrho v^3}\left(\frac{e^{-2\alpha_1 x} - e^{-\alpha_2 x}}{\alpha_2 - 2\alpha_1}\right)^2 \tag{2a}$$

where $I_2(x)$ intensity of acoustic wave with frequency 2ω at distance x from the transducer, $I_1(0)$ intensity of acoustic wave with frequency ω; q wave number of acoustic wave with frequency ω; α_1, α_2 attenuation coefficients of acoustic waves with frequency ω and 2ω respectively; Γ phonon-phonon coupling constant. This constant is expressed by elastic constants of the second and third order

$$\Gamma = (c_{jlpq}\delta_{ik} + c_{ijql}\delta_{kp} + c_{jkqp}\delta_{ip} + c_{ijklpq})\frac{\varkappa_j \varkappa_l \varkappa_q \gamma_i \gamma_k \gamma_p}{c_{ijkl}\varkappa_j \varkappa_l \gamma_k \gamma_l}, \tag{2b}$$

where c_{ijkl}, c_{ijklpq} elastic constants of the second and third order, respectively, γ_i, $\varkappa_j$ unit vectors in the direction of polarization and propagation of acoustic wave, δ_{ik} Kronecker delta. The Γ constant is very helpful in considering the attenuation of an acoustic wave in crystals.

The phonon-phonon coupling constant was determined from expression (2a) – intensity of light diffracted on acoustic waves with frequency ω and 2ω was measured and it was accepted that these intensities are proportional to adequate intensities of acoustic wave.

Measured values of the phonon-phonon coupling constant for a pure GaP crystal and GaP crystal with impurities are given in Table 4. Measurements were

Table 4. Phonon-phonon coupling constant

Direction	Impurity concentration m^{-3}	Γ	
[100]	pure	$3+\frac{c_{111}}{c_{11}}$	6 ± 2
	$1.9\cdot10^{24}$		7 ± 3
[110]	pure	$3+\frac{5c_{111}+3c_{112}+24c_{166}}{3c_{11}+2c_{12}+4c_{44}}$	4 ± 2
	$1.9\cdot10^{24}$		4 ± 2

carried out for a longitudinal wave in directions [100] and [110] at frequency of about 0.5 GHz. Also actual expressions for the phonon-phonon coupling constant in cubical crystals are given for these directions.

Hence, in the cause of experiments the influence of impurities on the phonon-phonon coupling constant was not stated. However, it should be added that the accuracy of determination of this constant was not very high about 50% and possible changes can be within the limit of error.

4. Interpretation of achieved results. Summary

The theoretical interpretation of achieved results is a rather complicated task and requires the consideration of the effect of electron gas, as well as of ions of impurities, on elastic properties of crystals. We will discuss the influence of electron gas on crystals elastic constants only and, hence, on propagation velocity and attenuation coefficient of an acoustic wave.

Figure 4 presents the band structure of GaP [4]. The energetic minimum in the conduction band is found in the direction [100] and its is achieved on the boundary of the Brillouin zone. Bacause there are six equivalent directions [100] then there six equivalent energetic minima. All energetic minima in a not deformed crystal are filled equally with electrons. Due to stress acting along one of the directions [100], the energy in two minima, which are parallel to this direction, increases by the value

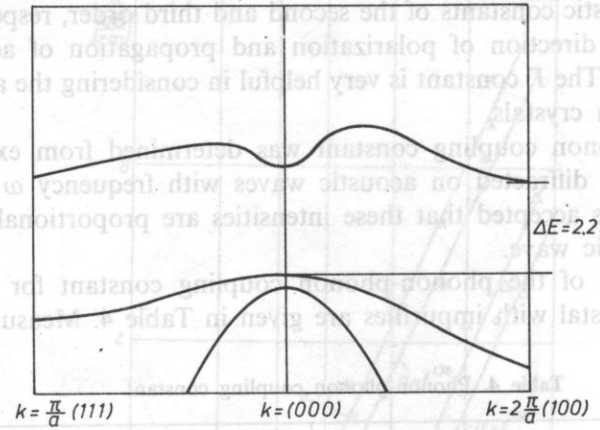

Fig. 4. Diagram of band structure of GaP

$2/3\phi$ and decreases in other four minima by the value $1/3s\phi$, where s is the deformation of the crystal caused by acoustic wave, ϕ deformation potential constant. This means that the number of electron decreases in two minima parallel to the direction of propagation and at the same time increases in four minima perpendicular to the direction of wave propagation. Changes of the number of electrons in individual minima lead to a decrease of their total energy. It can be proved [5] that the change of energy in the case under consideration is equal to

$$E = \frac{2}{9} n \frac{(\phi s)^2}{kT}, \tag{3}$$

where n — electron density, k — Boltzmann constant, T — temperature.

From a comparison of this expression with elastic strain energy $\frac{1}{2}\Delta c_{11} s^2$, we have a relationship between impurity concentration and change of adequate elastic constant c_{11} in this case

$$\Delta c_{11} = \frac{4n\phi^2}{9\,kT}. \tag{4}$$

Due to the arrangement of energetic minima in GaP, the energy of electrons during wave propagation in direction [111] changes equally in all directions, what results in

$$c_{44} = 0, \tag{5a}$$

$$c_{11} + 2c_{12} + 4c_{44} = 0, \tag{5b}$$

and correspondingly

$$c_{12} = -\frac{\Delta c_{11}}{2}. \tag{5c}$$

Measurements of propagation velocity of acoustic waves do not confirm above considerations fully.

Propagation velocity changes of an acoustic wave in direction [100] are indeed greatest, but also the velocity of a transverse wave in this direction undergoes changes. This proves that the constant c_{44} changes to be sure. These changes are smaller than changes of the constant c_{11} and occur in crystals with high concentration of impurities. Similar results were achieved in paper [6] from investigations of the influence of impurities on elastic properties of silicon.

While constant c_{12} slightly increases with the increase of impurity concentration.

It seems that the presence of ions of impurites in the crystal lattice is the main reason for mentioned divergences. These ions change interaction and, hence, elastic properties of the crystal.

From changes of the constant c_{11}, the value of the deformation potential constant was determined

$$\phi = \sqrt{\frac{9kT\Delta c_{11}}{4n}}. \tag{6}$$

When we substitute calculated values Δc_{11} for adequate values of impurity concentration, we obtain the following values of the deformation potential constant ϕ: 15.3 eV, 17.5 eV and 15.9 eV. The average is approximately 16 eV. It is a value of the same order as in other semiconductor materials.

Also intervalley transitions of electrons cause additional damping of the acoustic wave in crystals with impurities.

It appears [5] that wave damping due to intervalley transitions of electrons is expressed by

$$\Delta\alpha = \frac{\omega^2 \Delta c_{ij} \tau}{2\varrho v^3}, \tag{7}$$

where ω frequency of acoustic wave, Δc_{ij} change of elastic constants in direction under consideration, ϱ density τ relaxation time which characterizes intervalley transitions of electrons. Calculating the relaxation time from equation (7) we have

$$\tau = \frac{2\varrho v^3}{\omega^2 \Delta c_{ij}} \Delta\alpha. \tag{8}$$

Substituting achieved experimental results in the expression for a longitudinal wave in direction [100]: $\Delta\alpha = 2\text{dB/cm} = 23$ 1/m for $f = 10^9$ Hz, $\Delta c_{11} = 0.132 \cdot 10^{10}$ N/m^2, we have $\tau = 7.3 \cdot 10^{-13}$ s.

For other frequencies results of calculations are similar. Achieved values of relaxation times are too great in comparison with actual values, because attenuation increase in crystals with impurities is also caused by ions from impurities. Yet, an accurate analysis of this effect requires measurements at low temperatures when thermal ionization of impurities does not occur.

Summing up, we can say that a significant influence of impurities on acoustic

properties was stated in investigated crystals. The applied measurement method was accurate enough to determine changes of propagation velocity and acoustic wave attenuation coefficient in the considered range of impurity concentration. A full theoretical interpretation will be carried out when results of measurements in helium temperatures will be available.

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