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Виміряні нелінійні сприйнятливості третього порядку $\chi^{(3)}$ і коефіцієнт нелінійного поглинання в InAs n-типу з різним ступенем легування. Отримані значення $\chi^{(3)} \sim 10^{-7}$ СГСЕ істотно перевищують значення, обчислені на основі моделі, що описує нелінійну сприйнятливості електронів, які знаходяться в непараболічній зоні провідності. Показано, що спостережувана розбіжність усувається, якщо в розрахунку врахувати дисипації енергії електронів. Зростання ефективності при чотирьоххвильовій взаємодії в вузькозонних напівпровідниках обмежується нелінійним поглинанням взаємодіючих хвиль

Ключові слова: нелінійна сприйнятливості третього порядку, чотирьох хвильова взаємодія, вузькозонні напівпровідники, поріг пробоя

Измерены нелинейные восприимчивости третьего порядка $\chi^{(3)}$ и коэффициент нелинейного поглощения в InAs n-типа с разной степенью легирования. Полученные значения $\chi^{(3)} \sim 10^{-7}$ СГСЭ существенно превышают значения, вычисленные на основе модели, описывающей нелинейную восприимчивость электронов, находящихся в непараболической зоне проводимости. Показано, что наблюдаемое расхождение устраняется, если в расчете учесть диссипацию энергии электронов. Рост эффективности при четырехволновом взаимодействии в узкозонных полупроводниках ограничивается нелинейным поглощением взаимодействующих волн

Ключевые слова: нелинейная восприимчивость третьего порядка, четырехволновое взаимодействие, узкозонные полупроводники, порог пробоя

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A STUDY OF THE THIRD-ORDER NONLINEAR SUSCEPTIBILITY AND NONLINEAR ABSORPTION OF INAS IN THE MIDDLE INFRARED REGION

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1. Introduction

Nonlinear optical materials have numerous applications, including photodynamic therapy, nonlinear photonics, 3D optical data storage, frequency upconverted lasing, and fluorescence imaging [1–5]. One of the most important problems of applied nonlinear optics is the search for media with possibly large values of nonlinear susceptibilities. In this regard, semiconductors, as experiments have shown, are among the most promising media [6, 7]. The large nonlinearity of semiconductors basically comes from the fact that they, with their relatively small bandgap E_g , are characterized by sufficiently low internal fields, which determine the couple

forces acting on optical electrons. Therefore, even not too high laser fields should already provide a large contribution to the susceptibility of nonlinear electronic polarization.

2. Literature review and problem statement

The study of cubic susceptibilities is the central problem of nonlinear spectroscopy [8]. The effects due to the cubic susceptibility are the basis of such methods of nonlinear spectroscopy as two-photon spectroscopy, saturation spectroscopy and also allow solving such an important practical problem as the correction of phase distortions by the four-

wave mixing method (FWM) [9]. In the mid-infrared (IR) spectrum, where the most powerful and efficient lasers, including the CO₂ molecule, operate, the implementation of phase distortion correction by the wave front reversal method in four-wave mixing (WFR-FWM) with high efficiency is of particular interest. While nonlinear properties of most materials are studied in the visible and near infrared regions of the spectrum [5, 10–12].

In the work [10], using large-sized single crystals of high optical quality, the optical properties of Ba₂TiSi₂O₈ were systematically investigated, including transmission spectra, refractive indices and nonlinear absorption properties over a wide wavelength range from 340 to 2500 nm. In this experiment, the magnitude of $\chi^{(3)}$ was about 10⁻¹³ (esu), it is most likely related to electron cloud distortion [13]. The nonlinear optical properties of two graphene derivatives, graphene oxide and graphene fluoride, are investigated by means of the Z-scan technique employing 35 ps and 4 ns, visible (532 nm) laser excitation [14].

A study of nonlinear absorption in the infrared region was also carried out in narrow-band conductors [15–18]. These studies have shown that, because of the large value of linear and nonlinear absorption, semiconductors InSb and Hg_{1-x}Cd_xTe can not be used for reflection radiation at four-wave mixing in a wide range of radiation intensities. In this aspect, the narrow-gap InAs semiconductor has not been studied sufficiently.

3. The aim and objectives of the study

The aim is to search for and study media with high nonlinear susceptibility, also to investigate their characteristics that determine the maximum value of efficiency in four-wave interaction at a wavelength of 10.6 μ m.

To achieve the aim, let us consider the following objectives:

1. Investigation of the physical mechanism of nonlinear interaction in the InAs of the determining reflection in four-wave interaction at a wavelength of 10.6 μ m.
2. Identifying the parameters of nonlinear media influencing the efficiency of reflection.
3. The study of the temperature dependences of these parameters.

4. The measurements of breakdown threshold on the surface and constants of the nonlinear absorption in InAs

In the given work, InAs samples have been studied with various alloying degrees at room and nitrogen temperatures (Table 1).

For the entire application range of semiconductors, it is important to know the limit of their performance on the intensity of laser emission. This limit is usually imposed by the destruction threshold of the material. The source of radiation in our work was a pulsed TEA CO₂ laser operating in the lowest-order transverse mode TEM₀₀ mode. The duration of the generation pulse was ~150 ns at half-height of the front beam and approximately 1.5 μ s at the base. The measurements of the breakdown threshold on the surface of all samples studied in our work showed that this value lies within the range of 3–4·10⁷ Vt/cm². As shown by transmittance measurements in InAs samples unlike wide-bandgap

semiconductors (for example, Ge), noticeable reduction of transmittance is observed in the radiation intensity even lower than the breakdown threshold on the surface (Fig. 1).

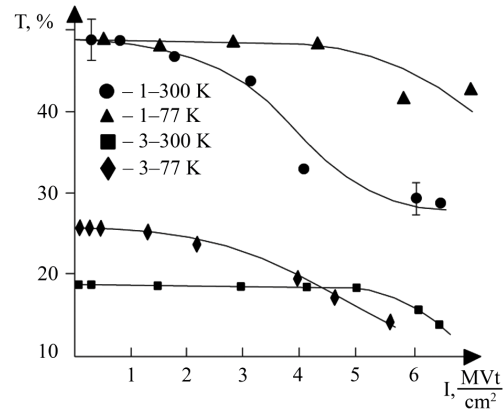


Fig. 1. Dependence of the transmittance T in samples of InAs No. 1 and 3 (with various values of N_e) on I at room and nitrogen temperatures. The curves represent the values calculated by (3)

Table 1

The main characteristics of the investigated samples InAs

Sample No.	Free electron concentration, $N_e \times 10^{17} \text{ cm}^{-3}$	Sample thickness l , cm	Free electron mobility μ , $10^4 \text{ cm}^2/\text{V}\cdot\text{s}$	Linear absorption coefficient α , cm^{-1} ($\lambda = 10.6 \text{ mkm}$)		Constant of nonlinear interaction M , cm/MVt	
				300 K	77 K	300 K	77 K
1	0.1	0.11	4.8	1	1	2.25	0.4
2	0.3	0.03	4	2.3	–	5.6	–
3	1.6	0.05	2.5	8.4	4	1.6	3.9
4	5.3	0.11	1.8	28	–	2.7	–

This transmittance decrease is reversible, manifests itself at radiation intensity $I \gtrsim 10^6 \text{ Vt}/\text{cm}^2$ and conditioned by the processes of nonlinear absorption of radiation in the researched semiconductors. Correlated values of the emission quantum of a CO₂ laser ($\hbar\omega \approx 0.117 \text{ eV}$) with bandgap InAs (0.35 eV) suggest that nonlinear absorption in them is conditioned by the three-photon process.

To determine from the data on the transmittance of the absorption constants, we will consider the problem of the dependence of transmittance on intensity, taking into account linear and nonlinear absorption. In the steady-state case, the change in intensity with the propagation of light through the semiconductors in the presence of three-photon absorption effects can be written as follows

$$-dI = \alpha I(x)dx + \eta I^3(x)dx + \delta I^4(x)dx, \quad (1)$$

where α is the linear absorption coefficient, η is the three-photon absorption coefficient, δ is the free hole absorption coefficient appearing as a result of three-photon absorption. δ is connected with η in the following ratio:

$$\frac{\delta}{\eta} = \frac{q\tau}{3\hbar\omega}, \quad (2)$$

where q is the absorption cross-section for the case of absorption by the free holes, τ is the lifetime of the nonequilibrium carriers. In $A^{\text{III}}B^{\text{V}}$ compounds, the absorption cross-section

by the free holes is so large [19] that even at moderate laser emission intensities the second term on the right-hand side of the equation (1) can be neglected. In this instance, the expression for transmittance of the samples based on three-photon absorption depending on the intensity of the incident emission I_0 takes the form:

$$T^{(3)} = (1-r)^2 \sqrt[3]{\frac{\alpha e^{-3\alpha l}}{\alpha + \delta I_0^3 (1 - e^{-3\alpha l})}}, \quad (3)$$

where r is the Fresnel reflection coefficient on the sample surface, l is the sample length.

Comparison of the results of experimental studies (Fig. 1) with the data of calculation by formulae (3) allows determining the values of δ directly. In view of the spread of the experimental data for InAs, the following is obtained:

$$\delta = 0.14 \pm 0.07 \text{ cm}^5 / \text{Mv}^3 \text{t}^3.$$

5. Nonlinear reflection in degenerate four-wave mixing

Four-wave mixing is the nonlinear process, in which the mixing of three waves in a nonlinear medium serves to generate a fourth wave (Fig. 2). The mechanism for the appearance of an inverted wave in such a scheme is most simply explained on the basis of a holographic interpretation of WFR [20]. Let an arbitrary wave $E_3(r)$ be incident on a nonlinear medium which needs to be reversed, and a reference wave $E_1(r)$ with constant amplitude over the cross-section. If the waves $E_1(r)$ and $E_3(r)$ are coherent, then they record the interference perturbations of the dielectric constant (hologram) in a nonlinear medium.

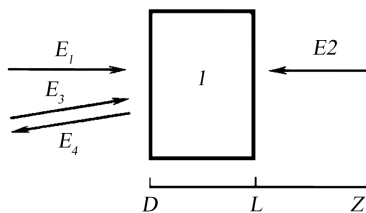


Fig. 2. A four-wave mixing scheme. 1 – nonlinear medium, E_1, E_2 – reference waves, E_3 – signal wave, E_4 – reflected wave, l – length of medium

If we illuminate this hologram from the opposite side by the wave $E_2(r)$ that is exactly counterpropagating to the reference wave $E_1(r)$ such that $E_2(r) = E_1^*(r)$, the hologram will reconstruct the reversal wave

$$E_4(r) = \text{const} \cdot E_1(r) E_2(r) E_3^*(r) = \text{const} \cdot |E_1|^2 E_3^*(r).$$

In a volumetric nonlinear medium, an interference pattern may also be written by the waves $E_2(r)$ and $E_3(r)$ and read by the wave $E_1(r)$ with the reconstruction of the same wave $E_4(r)$.

In this conventional scheme of WFR-FWM, the reflection coefficient R of the wave E_3 into the wave E_4 due to the intensity is connected with $\chi^{(3)}$ by the relation [20]:

$$R = |E_4 / E_3|^2 = |(4\pi\omega / cn)\chi^{(3)} E_1 E_2 \ell|^2, \quad (4)$$

where c is the speed of light in a vacuum, n is the linear refractive index, E_1, E_2 root-mean-square field strengths of reference waves, l is a length of the medium. In case when the

medium has a linear (α is the linear absorption coefficient on intensity) and nonlinear ($\gamma_n J^{n-1}$ is the nonlinear absorption coefficient on intensity) absorption under the condition $\gamma_n J^{n-1} \ll \alpha$ and in Born's approximation for R , the expression can be obtained [21]

$$R = 4M^2 I_1^2 e^{-2\alpha_{eff} l} \left(\frac{1 - e^{-\alpha_{eff} l}}{\alpha_{eff}} \right)^2, \quad (5)$$

where

$$\alpha_{eff} = \alpha + \gamma_n J^{n-1}.$$

Here γ_n is the constant of n -photon absorption,

$$M = \frac{\pi\omega\chi^{(3)}}{cn}$$

is the constant characterizing the nonlinearity of the medium.

From this expression, it follows that when only the linear absorption is taken into account, the dependence $R = f(I_1)$ must remain quadratic. The appearance of nonlinear absorption leads to growth restriction of R depending on I_1 , while for large I_1 it should lead to its decline.

The results of measurement of the dependence of R on I_1 in InAs samples have been shown in Fig. 3. With the growth of I_1 , R in both samples first increases quadratically, then R reaches a maximum value and decreases.

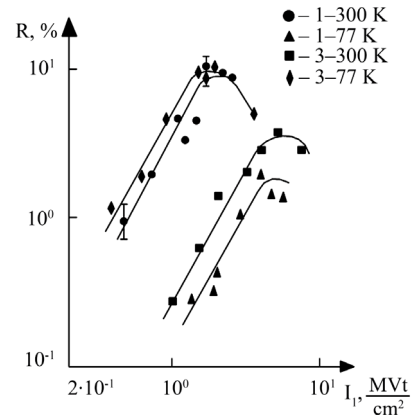


Fig. 3. Dependence of R on I in samples of InAs No. 1 and 3 at room and nitrogen temperatures. The curves represent the values calculated by (5)

6. The experimental determination of the third-order nonlinear susceptibility of InAs

The constant M , which characterizes the nonlinear coupling of the interacting waves, was determined for each sample from the formula (5) from the data on the measurements of the dependence of R on I_1 at small values of I_1 , when nonlinear absorption can be neglected and a quadratic dependence of R on I_1 is observed

$$M = \frac{\alpha\sqrt{R}}{2I_1 e^{-\alpha l} (1 - e^{-\alpha l})}. \quad (6)$$

It is known that the bandgap in the majority of semiconductors (these include InAs) increases with a drop in the temperature T [19]:

$$E_g(T) = E_g(0) - \frac{aT^2}{b+T}. \quad (7)$$

Here $E_g(0)$ is the bandgap when $T=0$ K, a and b are constants. In InAs $E_g(0)=0.426$ eV and the corresponding value $E_g(300\text{ K})$ is 0.35 eV ($\approx 3\hbar\omega_{CO_2}$). Thus, by cooling InAs ($a \approx 3.16 \cdot 10^{-4} \frac{\text{eV}}{\text{deg}}$, $b \approx 93$ K) to, for example, liquid nitrogen temperatures, $E_g(T=77\text{ K})$ compared to $E_g(300\text{ K})$ increases to 0.41 eV, which significantly exceeds $3\hbar\omega$, i. e., nonlinear absorption in InAs with a reduction in temperature may decrease noticeably.

Linear absorption in semiconductors is also a function of temperature, but the relation between α and T is highly dependent on the emission absorption mechanism. In case if absorption is caused by crystalline defects and foreign impurities, α practically does not depend on T . If absorption is due to free carriers, the relation between α and T is determined by the free carrier scattering mechanism [22] and practically for all scattering mechanisms α drops with a drop in temperature. The influence of the temperature on α and γ_n in InAs was investigated experimentally in samples No. 1 and 3. The results of the study of InAs sample No. 1 show that its linear absorption does not change with a drop in temperature ($\alpha \approx 1\text{ cm}^{-1}$). At the same time, the intensity of incident emission at which nonlinear absorption considerably manifested, increases from $\sim 1\text{ MVt/cm}^2$ at $T=300\text{ K}$ to $\sim 4\div 5\text{ MVt/cm}^2$ for $T=77\text{ K}$. The obtained results prove that linear absorption in this sample is conditioned by crystalline defects and foreign impurities. The reduction in nonlinear absorption is connected in this sample with an increase in the bandgap with a drop in temperature.

In contrast to sample No. 1, a noticeable drop (approximately 2 – fold from 8.4 to $\sim 4\text{ cm}^{-1}$) in linear absorption was revealed in sample No. 3. The intensity at which nonlinear absorption noticeably changes the transmittance of the sample with a drop in temperature also drops significantly. The observed variation in α with temperature in sample No. 3 is in good agreement with the theoretical dependence of emission absorption by free electrons on the temperature in the semiconductors [22]. Immutability of the nonlinear absorption constant in InAs sample No. 3 was unexpected. The reason for this effect, apparently, is due to the fact that donor impurity near the bottom of the conduction band with a sufficiently high concentration forms an impurity band. Its distance from the valence band is $E_{imp} < 3\hbar\omega_{CO_2}$ and has a weaker temperature dependence than E_g . Therefore, the nonequilibrium hole generation process in doped InAs can remain a three-photon process conditioned by the three-photon transfer of electrons from the valence band to the impurity band. It can be seen from Table 1 that a significant reduction in R with the drop in temperature in sample No. 1 is connected with the reduction in the constant M characterizing the nonlinearity of the medium by a factor of 5.5. In sample No. 3, M , vice versa, increased by a factor of 2.5 which together with the two-fold drop in the linear absorption caused an increase in R in InAs by a factor of ~ 30 (Fig. 3). The values of $\chi^{(3)} = \frac{cn}{\pi\omega} M$ obtained from the experimental data in InAs significantly exceed the values of $\chi^{(3)}$ in these semiconductors caused by the anharmonism of the motion of bound electrons (Table 2). On the other hand, it can be argued that the observed reflection by FWM is not connected with the generation of free carriers in three-photon

absorption in InAs. Otherwise, instead of the observed quadratic dependence of R on I_1 , $R \sim I_1^6$ in InAs would be observed. The contribution of the thermal nonlinearity mechanism to R , as evidenced by estimates, is insignificant ($< 0.05\%$). Thus, it can be assumed that the primary mechanism responsible for reflection in FWM in such semiconductors is the nonparabolic shape of the conduction band. Calculations of $\chi^{(3)}$ conditioned by the nonparabolic shape of the conduction band in semiconductors were carried out in classical work [23]. In Fig. 4, the dots represent the experimental data of $\chi^{(3)}$ obtained for various values of N_e and corresponding values of $\chi_{YUB}^{(3)}$ in InAs calculated in theory [23]. As it is shown in Fig. 4, the experimental values of $\chi^{(3)}$ differ significantly from $\chi_{YUB}^{(3)}$ and the increase in $\chi^{(3)}$ as a function of N_e is not monotonic, as it should follow from the theory.

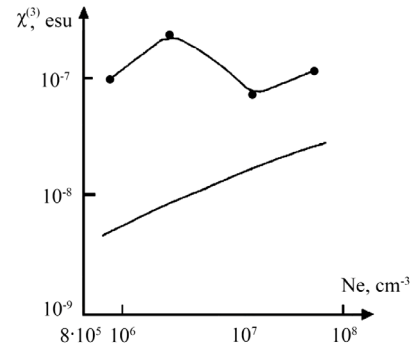


Fig. 4. Dependences of $\chi^{(3)}$ in InAs on the concentration of free electrons N_e (the solid curve represents the calculation from [9])

At low carrier concentrations ($N_e \leq 3 \cdot 10^{16}\text{ cm}^{-3}$), the ratio $\chi^{(3)} / \chi_{YUB}^{(3)}$ is $\sim 20\div 30$ and with an increase in N_e it drops, and when $N_e \gtrsim 1.6 \cdot 10^{17}\text{ cm}^{-3}$, this ratio is $4\div 6$. The maximum value of $\chi^{(3)} \approx 2.5 \cdot 10^{-7}\text{ esu}$ in InAs was observed in a sample with $N_e \approx 3 \cdot 10^{16}\text{ cm}^{-3}$.

7. Discussion of the results of investigating the mechanism of the third-order nonlinear susceptibility in InAs

The observed difference of the measured values of $\chi^{(3)}$ and $\chi_{YUB}^{(3)}$ may be related to the following fact. The current scheme for calculating nonlinear optical susceptibilities is based upon an expansion of the density matrix of a system consisting of the matter and the electromagnetic field into a series in terms of perturbation theory. For electron polarization, the expansion parameter in perturbation theory is E/E_{at} . In this case, the change in the distribution function of the electrons in the system is neglected.

Accounting for the change in the distribution function, for nonlinear optical degenerate effects in the expansion of polarization in terms of the field powers results in parameters other than E/E_{at} and even significantly exceeding it. It is these parameters that give rise to the significant and even "giant" nonlinearities in the interaction of emission and matter. Therefore, significant nonlinearities can be observed in the response of the matter to macroscopic changes introduced under the field action (the generation of current carriers in the semiconductors, absorption saturation, changes in the system of energy levels, etc.) and accompanying irreversible changes in the system.

In particular, the study [24] demonstrates that accounting for the energy dissipation of free electrons due to

interaction with the crystalline lattice, impurity ions, etc., the nonlinear susceptibility conditioned by the nonparabolic shape of the conduction band in degenerated FWM can considerably exceed $\chi_{yub}^{(3)}$

$$\chi^{(3)} = 2 \cdot \frac{\tau_E}{\tau_p} \cdot \chi_{yub}^{(3)},$$

where τ_p is the momentum relaxation time, τ_E is the energy relaxation time.

Table 2 shows experimentally measured values of $\chi^{(3)}$ and $\chi_{yub}^{(3)}$ for the corresponding N_e . From the ratio of these quantities, the values of τ_E/τ_p have been determined. The values of

$$\tau_p = \frac{m_e^* \mu}{e}$$

calculated from the mobility data μ , and also the values of τ_E determined from the data on τ_E/τ_p and τ_p are presented.

Table 2
Experimentally measured values of $\chi^{(3)}$ and $\chi_{yub}^{(3)}$ for samples with various degrees of doping

N_e, cm^{-3}	10^{16}	$3 \cdot 10^{16}$	$1.6 \cdot 10^{17}$	$5.3 \cdot 10^{17}$
$\chi^{(3)}, \text{esu}$	$1.01 \cdot 10^{-7}$	$2.52 \cdot 10^{-7}$	$0.72 \cdot 10^{-7}$	$1.21 \cdot 10^{-7}$
$\chi_{yub}^{(3)}, \text{esu}$	$4.9 \cdot 10^{-9}$	$8 \cdot 10^{-9}$	$1.7 \cdot 10^{-8}$	$2.2 \cdot 10^{-8}$
τ_E/τ_p	10.3	15.8	2.1	2.7
τ_p, ps	0.8	0.65	0.4	0.2
τ_E, ps	8.2	10.3	0.8	0.54

The obtained data τ_E/τ_p and τ_E in InAs coincide in order of magnitude with the characteristic values of these quantities in semiconductors [22]. Scattering mechanism of carriers (ionized impurity scattering, dislocations, optic and acoustic vibrations, etc.) is significantly affected by the relaxation time τ_E and τ_p .

The table shows that with an increase in electron concentration (and correspondingly concentration of impurity ions), the momentum relaxation time τ_p decreases. Such a behavior of τ_p depending on N_e indicates that an increase in the impurity concentration enhances the scattering effect. The observed dependence of τ_E/τ_p on N_e is apparently related to the fact that τ_E decreases with increasing N_e more rapidly than τ_p .

It is known that the band structure in InAs is well described by the Kane model [22] and the conduction band structure can be described as

$$E(k) \sim \frac{\hbar^2 k^2}{4m_e^*} - \frac{\hbar^2 k^4}{4(m_e^*)^2 E_g}, \quad (8)$$

where k is the wave vector of an electron. According to this expression, the major contribution to the nonlinear susceptibility $\chi^{(3)}$ caused by the nonparabolic shape of the conduction band is given by electrons with large k . With decreasing temperature, the number of such electrons decreases, and electrons accumulate at the bottom of the conductivity zone near the minimum (for $k=0$), where the second term in the expressions (8) is negligible. Apparently, the observed decrease in the sample $\chi^{(3)}$ with $N_e \approx 2 \cdot 10^{16} \text{ cm}^{-3}$ at $T \approx 77 \text{ K}$ relative to $\chi^{(3)}$ at 300 K is due to this circumstance insofar as at $T \approx 77 \text{ K}$ the effective density of states in the conduction band $N_{eff} \sim 2 \cdot 10^{16} \text{ cm}^{-3}$ and the accumulation of all electrons near the minimum of the conduction band by the Pauli principle are still not forbidden. With increasing N_e , the accumulation of electrons in the region k , where the second term is insignificant, is hampered in accordance with the Pauli principle. It can, therefore, be expected that for large N_e , the decrease in $\chi^{(3)}$ with temperature will not be as strong as for $N_e \approx 2 \cdot 10^{16} \text{ cm}^{-3}$. Indeed, as experiments have shown, in the sample with $N_e \approx 1.6 \cdot 10^{17} \text{ cm}^{-3}$, $\chi^{(3)}$ not only did not decrease, but even increased. This growth, apparently, is due to the fact that the thermal velocity of the charge carriers decreases with a decrease in temperature of the crystal. In the case, when the main mechanism is scattering by impurity ions, a decrease in the thermal velocity of carriers leads to an increase in the interaction of charge carriers with ionized impurity atoms, since the duration of the interaction increases and decreases τ_p .

8. Conclusions

As a result of the research:

1. It is shown that the narrow-gap semiconductor InAs has a high value of nonlinear susceptibility $\chi^{(3)} \approx 10^{-7} \text{ esu}$ and allows getting the high efficiency of four-wave mixing.
2. It is determined that the primary mechanism responsible for reflection in four-wave mixing in such semiconductors is the nonparabolic shape of the conduction band.
3. Nonlinear absorption is the main limiting factor in the growth of reflection efficiency in four-wave mixing with increasing radiation intensity.

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