საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 12, №3, 2018
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 12, no.3, 2018

Physics

Exponential Optical Absorption in Non-Irradiated and Irradiated III-V Compounds

Nodar Kekelidze[*], Bela Kvirkvelia[*], David Kekelidze[*], Elza Khutsishvili[*], Lali Nadiradze[**], George Kekelidze[§], Tengiz Qamushadze[*], Zurab Chubinishvili[§§], Ia Kalandadze[§§]

[*]*Semiconductor Materials Science Laboratory, Ferdinand Tavadze Institute of Metallurgy and Materials Science, Tbilisi, Georgia*
Substance Research Institute, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia
[**]*Tbilisi Classical Gymnasium,Tbilisi, Georgia*
[§]*BoT EUROSOLAR, e.V.Bonn 53113, Germany*
[§§]*Faculty of Informatics and Control System, Georgian Technical University, Tbilisi, Georgia*

(Presented by Academy Member Nodar Tsintsadze)

ABSTRACT. The dependence of the optical absorption coefficient vs photon energy near fundamental absorption edge for InP, InAs and InP-InAs solid solutions was studied. The experiments were performed at T=300K and T=80K before and after irradiation with high energy electrons (50MeV). Before and after irradiation there has been revealed the exponential dependence of the optical absorption coefficient vs photon energy with energy deficiency at all temperatures and in all cases of irradiation. The mechanism of this phenomenon and the quantitative calculations, which are in agreement with experimental data, were implemented. For the irradiated crystals picture gets complicated. For crystals irradiated with high-energy electrons (50MeV), quantitative analysis of the results is performed. It was shown that in irradiated crystals the exponential tails are the result of the action of point defects.

Key words: semiconductors, exponential absorption, irradiation, point defects

Exponential optical absorption found at the fundamental edge is not something exclusive. It is a general phenomenon clearly observed in many semiconductors. This phenomenon is very prominent in III-V compounds. It was found in the irradiated materials as well. Nevertheless, identification of the mechanism and development of general theory that would allow specific quantitative calculations turned out to be a significant problem. This issue is of great importance for development of the new generation optoelectronic devices. On the other hand, study of the irradiated materials is of importance for creation of the optical structures and photocells that effectively operate in the space and at nuclear plants. This work is dedicated to research of the mentioned issue on the example of InAs, InP compounds and InP_xAs_{1-x} solid solutions.

InP and InAs are important materials for use in optoelectronics, microelectronics and nanotechnologies because of their high mobility of electrons and direct energy bands. On their basis, photocells with quantum dots with a high conversion coefficient, as well as nanostructures, etc. are manufactured [1-3].

We have shown that InAs-InP solid solutions possess unique radiation properties, allowing discovery of the phenomenon of mutual compensation of radiation donors and acceptors, and development of materials that withstand very high fluencies of hard irradiation [4-12].

Experiments

Monocrystals of InAs, InP and practically all required compositions of InP_xAs_{1-x} solid solutions were grown using the horizontal zone melting method. The obtained semiconductor materials are characterized by a very high degree of homogeneity. The frequency dependences of the optical absorption coefficient near the fundamental edge of these crystals have been measured before and after irradiation by electrons with energies E=50MeV to fluencies of $\Phi=6\cdot10^{17}$el/cm^2 and fast neutrons with $\Phi=2\cdot10^{18}$n/cm^2. The optical measurements were carried out at room temperature and at T=80K using an infrared spectrometer and an optical cryostat.

Results and Discussion

Optical absorption near the fundamental edge before irradiation. The frequency dependences ($h\nu$) of the optical absorption coefficient (K) in the long-wave fundamental absorption region have been measured in InAs, InP crystals and their InP_xAs_{1-x} solid solutions. The results before irradiation are shown in Fig. 1. [lnK=f($h\nu$)]

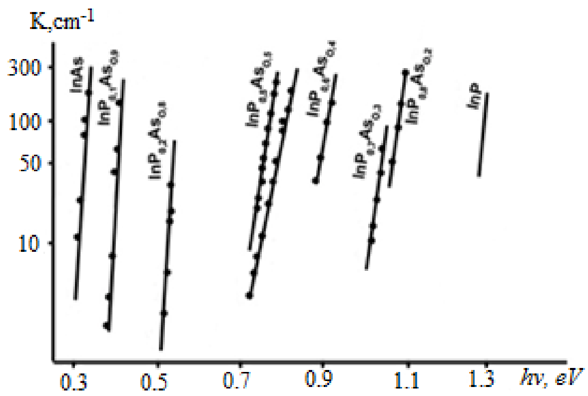

Fig. 1. The dependence of the optical absorption coefficient on the photon energy in InAs, InP and InP_xAs_{1-x} solid solutions before irradiation.

It is shown that the presented dependence is described by an exponential law:

$$K=A_0e^{h\nu/E_0}, \quad (1)$$

Where E_0 is the parameter characterizing the material.

Absorption occurs at energies less than the forbidden band width. This phenomenon is anomalous also, due to the fact that according to the classical theory of semiconductors the dependence $K(h\nu)$ should be expressed as an indicative function:

$$K\sim(h\nu-E_g)^n, \quad (2)$$

Where Eg is the width of the forbidden band.

It is shown that the regularity of (1) is invariably observed at both high and low temperatures and is preserved when the concentration of the impurity is varied over a wide range. This regularity was also found in irradiated crystals.

The dependence (1) is called Urbach's law [13],

$$K=A_0 e^{h\nu/k_0T}, \tag{3}$$

where k_0 is the Boltzmann constant, T is the temperature.

This law was discovered by the author [13] in ionic crystals. However, in semiconductors the situation is much more complicated. There E_0 (see relation 1) is not equal to k_0T and, moreover, it depends on the impurity concentration. Incidentally, it turned out that even in ionic crystals T differs from the true temperature of the sample.

The exponential dependence (1) was also found in many other semiconductors, offering that the observed phenomenon is not an exception, but rather a general law. It is believed that in ionic crystals, Urbach's law is the result of the interaction of electrons with many phonons and that the process is realized through excitons absorption. We have shown that excitons in semiconductors do not form the Urbach tails of absorption. In general, very complex processes occur in semiconductors, which makes it difficult to develop a general mechanism, moreover, in the works of a number of authors, inaccuracies and even obvious errors have been revealed.

It was believed that the physically and mathematically well-grounded mechanism of this phenomenon was developed by the well-known researchers Dixon and Ellis [14]. In [15] the theory and mechanism of Dixon and Ellis were confirmed.

Authors [14] result is a consequence of the presence of a temperature smearing of the Fermi distribution. It follows from the Dixon and Ellis theory that in heavily doped crystals, the E_0 value (1) depends on the temperature, and does not depend on the impurity concentration, and in the weakly doped crystals, the reverse picture takes place.

We have experimentally and theoretically proved that in reality, everything is reverse: in heavily doped crystals, E_0 does not depend on temperature while in weakly doped crystals it does.

Other theoretical models have been developed in [17, 18], which are too limited. N. Kekelidze and his co-workers [19-21] developed mechanism of the phenomenon: in the general case, the observed phenomenon is the result of superimposing of two processes of the phonon broadening of the edge and the appearance of tails of the density of states in the forbidden band. Both these processes are described by exponential frequency dependence.

At relatively high temperatures (including room temperature) in relatively pure crystals, this phenomenon is determined by the interaction of carriers with longitudinal optical phonons and the slope of the curves - (E_0) is proportional to the temperature.

As the temperature is lowered, the effect of phonon interaction with electrons sharply decreases and below 77K ceases to play a noticeable role. Under these conditions, the phenomenon is mainly determined by impurities, more precisely by the fluctuation of charged impurity concentrations and the influence of the corresponding tailings of the density of states. The value of E_0 is independent of temperature and is proportional to the concentration of ionized impurities. In intermediate cases, both processes are important.

Based on the developed mechanism, it is possible to explain well all the available results, both ours and of the other authors. We have also achieved a quantitative agreement between the theoretical calculations and our experimental results. The phonon interaction with electrons processes were calculated using Dunn's theory [22]. For InAs, at T=300K, the experimental value E_0=(8÷10)·10^{-3}eV, which is in excellent agreement with the theoretical value E_0=10·10^{-3}eV. At low temperatures, the experiment yields E_0=1.5·10^{-3}eV, and on the basis of calculations E_0=1.2·10^{-3}eV.

Well-coordinated data were also obtained for solid solutions. The experiment accurately captures the growth of longitudinal optical phonons values in the transition from InAs to InP, which is caused by an increase in the magnitude of the longitudinal optical phonon, which in turn is due to an increase in the degree of ionicity in the chemical bond of the compound with an increase in the amount of phosphorus in the alloy.

For InP at 300K, the experiment yields E_0=16·10^{-3}eV, and the theory E_0=14·10^{-3}eV.

Optical absorption near the threshold in irradiated crystals. A quantitative analysis of frequency dependence of optical absorption coefficient $K(h\nu)$ near the band-edge in InAs and InP crystals, irradiated with 50MeV electrons has been carried out. Results are presented in Table.

Table. Quantitative analysis of frequency dependence of optical absorption coefficient *K*(*hν*) near the band-edge in InAs and InP crystals, irradiated with 50MeV electrons

#	compound	Carriers concentration before irradiation cm^{-3}	type	Before irradiation		$2\cdot10^{16}$ e/cm^2	$4.5\cdot10^{16}$ e/cm^2	$1\cdot10^{17}$e/cm^2		$4\cdot10^{17}$e/cm^2		$6\cdot10^{17}$e/cm^2		annealing at 200^{0}C	annealing at 500^{0}C	
				300K	80K	300K	300K	300K	80K	300K	80K	300K	80K	300K	300K	80K
1	InAs	$2.0\cdot10^{16}$	n	8.0		9.0	10.0					27.0	22.0	17.0	8.0	
2	InAs	$3.0\cdot10^{16}$	n	8.3						16.2	12.5					
3	InAs	$1.7\cdot10^{17}$	n	8.4				13.5	15.4						9.0	
4	IAs	$2.0\cdot10^{17}$	n	10.0	6.4					23.0	14.0				14.2	10.5
5	InP	$1.1\cdot10^{16}$	n	18.5		30.0						54.0		65.0	19.0	

The table above provides measured values of the characteristic parameter E_0 (without 10^{-3}eV) for InAs and InP samples before and after irradiation of the crystals. Crystals were irradiated with 50MeV electrons within the interval from $2\cdot10^{16}$e/cm^2 to $6\cdot10^{17}$e/cm^2. Measurements were made at T=300K and T=80K temperatures. The samples were also annealed at 200^{O}C and 500^{O}C temperatures. The table provides also the carriers concentrations before irradiation. Interesting regularities were found.

For the weakly doped InAs, at room temperature, before crystal irradiation E_0=8, accurately reflects the effect of longitudinal optical phonons. Weak irradiation with fluencies of $\Phi=2\cdot10^{16}$e/cm^2 and $\Phi=4.5\cdot10^{16}$e/cm^2 causes radiation defects resulting in weak yet noticeable growth of E_0, from E_0=9 to E_0=10. Irradiation of the samples with maximal fluence of $\Phi=6\cdot10^{17}$e/cm^2 resulted in drastic growth to E_0=27.0 at the room temperature while at 80K value of E_0 reduced slightly to E_0=22.0, caused by dramatic reduction of the phonons' action. E_0=22.0 value actually reflects the effect of radiation defects. Crystal annealing at 200^{0}C temperature reduces number of radiation defects as clearly seen from E_0 reduction to 17, while annealing at 500^{O}C fully restores the crystal. The defects eliminate and E_0 regains its original value. In sample #2, where the concentration of the doping impurities was slightly higher than in crystal

#1, approximately similar process takes place. In addition, even the mentioned slight change is reflected in increase of E_0, to 8.3. In Sample #3, with growth of electrons' (impurities') concentration E_0 increases to 8.4 while in the conditions of significant irradiation ($\Phi=1\cdot10^{17}e/cm^2$) E_0 achieves 13.5.

Sample #4, with increased doping and hence concentration of electrons ($n=2\cdot10^{17}$) E_0 value increases to 10. Similar to the case of radiation defects, based on the E_0 values we can assess growth of impurities' concentration. Irradiation with $\Phi=1\cdot10^{17}e/cm^2$ fluence increases number of defects and hence E_0 values, to reach 23 (T=300K) and 14 (T=80K) respectively. Thermal treatment (T=500^{O}C) did not result in full restoration of the defects, providing E_0=14.2.

As we can see from the table, results for InP samples are quite different. All values are increased significantly. The crystal contains low concentration of impurities, as a result, value of the characteristic parameter shows the effect of lattice vibration E_0=18.5, significantly higher, compared with InAs. This is caused by increase of longitudinal optical phonon value. Irradiation with even minimal fluence of the electrons ($\Phi=2\cdot10^{16}e/cm^2$) results in significant growth of E_0=30 while maximal fluence provides high value of E_0=54.

All above is caused by the fact that phosphorus weight is two times lower than arsenic weight as a result its lattice damage is much severer and hence contains much more radiation defects, compared with InAs.

Results of heat treatment of the irradiated crystal at T=200^{O}C are very interesting, In InP E_0 value does not fall, rather, it grows significantly to E_0=65. The cause is that irradiation with significant fluencies create large defects in InP though they are not optically and electrically active. We regard that the studied fundamental absorption long-wave exponential tails result from the point radiation defects rather than from their large associations. In the conditions of thermal treatment these associations split to produce active point defects, causing growth of E_0. Thermal treatment at 500^{O}C restores the crystal lattice as evidenced from the value E_0=19.

Based on the performed studies we can conclude that E_0, the parameter characterizing fundamental optical absorption exponential tails is particularly sensitive to radiation defects, similar to the impurities. And this provides significance information about radiation defects and impurities, clarify the mechanisms of defects emergence through analysis of the E_0 values.

Conclusion

In InAs, InP crystals and their InP-InAs solid solutions, the exponential frequency dependences of the optical absorption coefficient near the fundamental edge were studied at room and low temperatures, before and after irradiation with electrons. The mechanisms of this anomalous phenomenon were developed. The quantitative analysis of the results has been performed. It was shown, that in irradiated crystals the exponential tails are results of point defect action.

This work was supported by Shota Rustaveli National Science Foundation (SRNSF) [Grant #YS-2016-74, Project Title: Application of Arsenic of Georgian Ores for Producing Crystals of III-V Semiconductor Compounds].

ფიზიკა

ექსპონენციალური ოპტიკური შთანთქმა დაუსხივებელ და დასხივებულ III-V შენაერთებში

ნ. კეკელიძე*, ბ. კვირკველია*, დ. კეკელიძე*, ე. ხუციშვილი*, ლ. ნადირაძე**, გ. კეკელიძე§, თ. ქამუშაძე*, ზ. ჩუბინიშვილი§§, ი. კალანდაძე§§

**ფერდინანდ თავაძის მეტალურგიისა და მასალათმცოდნეობის ინსტიტუტი, ნახევარგამტარული მასალათმცოდნეობის ლაბორატორია, თბილისი, საქართველო*

**ივანე ჯავახიშვილის სახელობის თბილისის სახელმწიფო უნივერსიტეტი, ნივთიერებათა კვლევის სამეცნიერო კვლევითი ინსტიტუტი, თბილისი, საქართველო*

***თბილისის კლასიკური გიმნაზია, თბილისი საქართველო*

§BoT EUROSOLAR, e.V.Bonn 53113, გერმანია

§§საქართველოს ტექნიკური უნივერსიტეტი, თბილისი, საქართველო

(წარმოდგენილია აკადემიის წევრის ნოდარ ცინცაძის მიერ)

შესწავლილია ოპტიკური შთანთქმის კოეფიციენტის დამოკიდებულება ფოტონის ენერგიაზე ფუნდამენტური შთანთქმის კიდის მახლობლად **InP, InAs** და მათი **InP-InAs** მყარი ხსნარებისთვის. ექსპერიმენტები ტარდებოდა **T=300K** და **T=80K** ტემპერატურაზე, დასხივებამდე და მაღალი ენერგიის ელექტრონებით **(50MeV)** დასხივების შემდეგ. დასხივებამდე და დასხივების შემდეგ გამოვლინდა ოპტიკური შთანთქმის კოეფიციენტის ფოტონის ენერგიაზე ექსპონენციალური დამოკიდებულება ენერგეტიკული დეფიციტით ნებისმიერ ტემპერატურაზე და დასხივების ყველა შემთხვევაში. დამუშავებულ იქნა ამ მოვლენის საერთო მექანიზმი და ჩატარებულ იქნა რაოდენობრივი გათვლები, რომლებიც კარგ თანხვედრაშია დაუსხივებელი მასალების ექსპერიმენტულ მონაცემებთან. დასხივებული კრისტალებისთვის სურათი რთულდება. ჩატარებულია რაოდენობრივი ანალიზი მაღალი ენერგიის **(50MeV)** ელექტრონებით დასხივებული კრისტალებისთვის. ნაჩვენებია, რომ დასხივებულ კრისტალებში ექსპონენციალური კუდები არის წერტილოვანი დეფექტების ზემოქმედების შედეგი.

REFERENCES

1. Jiang X., Xiong Q., Nam S., Qian F., Li Y., and Lieber Ch. M. (2007) InAs/InP Radial Nanowire Heterostructures as High Electron Mobility Devices. Nano Lett. 7, 3214.: 3214.
2. Roddaro S., Pescaglini A., Ercolani D., Sorba L, and Beltram F., (2011) Manipulation of electron orbitals in hard-wall InAs/InP nanowire quantum dots. Nano Lett. 11(4).:1695.
3. Stokes D. W., Li J. H., Forrest R. L., Ammu S. L., Lenzi J. C., Moss S. C., Nosho B. Z., Aifer E. H., Bennett B. R., and Whitman L. J., (2004) Optical and structural properties of InAs/GaSb nanostructures. Mater. Res. Soc. Symp. Proc., vol. 794, no. T9.:9.
4. Kekelidze N., Kekelidze G., Kekelidze D., Aliyev V. (2012) Investigation of InP_xAs_{1-x} solid solutions and creation of the radiation-resistant materials on their basis. AIP-Proceedings of International Conference on the Physics of Semiconductors –ICPS. Zurich, 1566.:101.
5. Kekelidze N., Kvirkvelia B., Kekelidze D., Khutsishvili E., Kekelidze G. (2014) Phenomenon of Mutual Compensation of Radiation Donors and Acceptors and Creation of Radiation-Resistant Materials. Journal of Electrical Engineering, 2, #4.:187.
6. Khutsishvili E., Kvirkvelia B., Kekelidze D., Aliyev V., Khomasuridze D., Kekelidze N. (2012), Carriers mobility of InAs and InP- rich InAs-InP solid solutions irradiated by fast neutrons. AIP-Proceedings of International Conference on the Physics of Semiconductors. Zurich. 1566.:103.
7. Kekelidze N., Khubua J., Kekelidze G., Kekelidze D., Aliyev V., Kvirkvelia B., Khutsishvili E. (2013) Radiation-resistant Semiconductor Materials for Application on Accelerators, Nuclear Reactors and in Space Proceedings of the 7th International Conference "Physics in the LHC era".:59.
8. Kekelidze N., Khutsishvili E., Kvirkvelia B., Urushadze G., Kekelidze G. Transport Properties in Solid Solutions of InP & InAs Semiconducting Compounds. (2014) Abstract of 32nd International Conference on the Physics of Semiconductors. Austin, USA.
9. Kekelidze N., Khutsishvili E., Kvirkvelia B., Urushadze G. and Kekelidze. G. Current Carriers Scattering in InP-InAs Solid Solutions. (2014) Journal of Electrical Engineering JEE. 2, #2:86.
10. Kekelidze N., Khutsishvili E., Kvirkvelia B., Kekelidze D., Alijev V., Kekelidze G. Transport Properties of InAs-InP Solid Solutions. (2014) Journal of Electrical Engineering JEE. 2, #5.:207.
11. Kekelidze N., Khutsishvili E., Kvinikadze Z., Davitaja Z., Kekelidze D., Kvirkvelia B., Sadradze K., Nadiradze L., Kekelidze G. (2017) Nanosize Clusters in InAs and InP Compounds and Their Solid Solutions $InP_xAs_{1–x}$. American Journal of Nano Research and Applications. 5(3-1).:48.
12. Kekelidze N., Kekelidze D., Khutsishvili E., Kvirkvelia B., Kobaidze R., Kekelidze G. (2018). Semiconductor Materials Withstanding Large Fluence of Hard Irradiation. Proceddings of International Conference on Applied Physics and Mathematics. Brussels. p. 7-11.
13. Urbach F. (1953) The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids. Phys.Rev., 92.: 1324.
14. Dixon J .R., Ellis J.M. Optical Properties of n-Type Indium Arsenide in the Fundamental Absorption Edge Region. (1961), Phys.Rev., 123.:1560.
15. Zotova N.V., Nasledov D.N., Neuimina L.D. (1971) The absorption edge of n-InAs at 300 and 100K. Fiz. Tekh.Poluprovodn. 5. #11.:2111.
16. Kaiser, W., Fan H.Y. Infrared Absorption of Indium Antimonide, (1955) Phys.Rev., 98.: 966.
17. Redfild D. (1963) Effect of defect fields on the optical absorption edge, Phys.Rev., 130.:916.
18. Dow J.D and Redfield D. (1972) Toward a unified theory of Urbach's rule and exponential absorption edge, Phys.Rev. B, 5,:594.
19. Kekelidze N., Salukvadze T., Tsinadze N., Koridze V. (1970) Functional form of absorption near the threshold in InAs, InP, and in InP_xAs_{1-x} alloys. Proceedings of the Tbilisi State University, 135.
20. Kekelidze N.P., Kekelidze G.P., Tsinadze N.M., Makharadze Z.D., Gelovani E.M. and Shatberova E.B. (1971) Electrical properties of InP-InAs crystals and their InP_xAs_{1-x} solid solutions, Abstracts of the All-Union Conference on Electrical and Optical Properties of A3B5-type Crystal, Ashkhabad, 167.
21. Kekelidze N.P., P.Kekelidze G. (1972) Optical Absorption near the Threshold in n-Type InP, InAs Crystals and their InP_xAs_{1-x} solid solutions. Phys.Lett. 42A, №2, :129.
22. Dunn D. (1968) Urbach's Rule in an Electron-Phonon Model, Phys. Rev. 174, :855. © 2018 Bull. Georg. Natl. Acad. Sci.

Received May, 2018