Laser Raman-Spectroscopy Study of Fundamental Optical Properties of Some of A^3B^5 and A^2B^6 Type Semiconductors and Influence of Ion Implantation on These Raman-Spectra

Dissertation for degree of a Doctor of Physical-mathematical sciences

Author Sergo V. Gotoshia

2008, Georgia, Tbilisi

R e s u m e

In the first chapter the current state of laser Raman spectroscopy study of semiconductors in the world is given in the form of literary review. The cited literature generally relies both on the experimental data given in the Dissertation and the necessary materials used with the purpose of theoretical analysis.

In the second chapter the Raman scattering essence, the theory very generally and briefly is given mainly from the practical point of view.

In the third chapter the dynamics of Raman spectroscopy progress in the world is given in details from its discovery up to day.

The fourth chapter includes the detailed description of laser Raman systems I first have constructed in Georgia, the principles of instrument-making I first started in laser Raman spectroscopy direction, bases of the Dissertation and other investigations.

In the fifth chapter the problems of identification-classification of phonon types in semiconductors are investigated on the ground of theoretical-group consideration and experimental data comparison. This process was carried out in case of natural mineral, α-HgS. The first order phonon frequencies have been determined and these phonons' classification has been made on the basis of the polarization measurements. The minerals under investigation were from various geological mines of Georgia and other countries. The minerals from certain mines contained isomorphic impurity, selenium, in various concentrations. The gap vibration corresponding to this impurity was first found by Raman spectroscopy, gap vibration frequency of selenium impurity was determined. On the basis of these investigations a method of identification of geological mines of cinnabar with the aid of Raman spectroscopy is suggested, as well as the utilization of these data to state the origin of mineral pigment dyes, which is very important for studying as well as for conservation of ancient and medieval art pieces.

With the aid of Raman spectra we also found the gap vibration of arsenic in GaP when in GaP there is a big amount of arsenic substituted izomorphically.

The third system, in which we found local vibrations of aluminum impurity with the aid of Raman spectra, is GaP:Al.

The sixth chapter in the Dissertation is dedicated to the analysis of semiconducting ternary mixed crystals. Generally the mixed crystals are solid solution formed by isomorphic substitution of two individual sub-lattices. It is stated theoretically that in such crystals behavior of LO and TO phonons mainly is subjected to the rules of two types, one-mode and two-mode behavior. Accordingly the mentioned crystals are called crystals of one-mode and two-mode behavior.

We investigated three various systems: $GaAs_{1-x}P_x$, $Ga_{1-x}Al_xP$ and $ZnTe_{1-x}Se_x$. The first two are of A^3B^5 type, the third belongs to the A^2B^6 system.

The system $GaAs_{1-x}P_x$ represented films growing epitaxially on substrates GaAs and GaP. Their orientation was (001) and therefore we fixed only longitudinal LO phonons with Raman reflection configuration. We ascribed the mentioned system to the crystals of two-mode behavior. One of the facts proving this is the formation of gap vibration by doping heavy isomorphic impurity As in sublattice GaP observed in Raman spectrum. We spoke about this fact above. We were the first to study this system by Raman scattering reflecting configuration, when laser exciting wave penetrated only some hundreds nanometer depth in the epitaxial film layer. This fact is very important from the practical point of view, for instance, for quantitative analysis of the same compound synthesized by ion implantation.

The second system $ZnTe_{1-x}Se_x$ was bulk crystals as cubes polished optically. The peculiarity of our investigation is that besides volume excitation this system has been studied in resonance conditions too. As a result besides the first order phonons the high order phonons have also been fixed. The phonons' repetition is observed against a background of extensible photoluminescence. The system $ZnTe_{1-x}Se_x$ was ascribed to one-mode crystals. The corresponding concentration graphs have been plotted.

The third system, $Ga_{1-x}Al_xP$ we have first studied by various wavelengths excitation of laser, represented epitaxial films, growing on substrate GaP. The substrate orientation was (001) generally. In this case too the Raman scattering occurred with reflection configuration and only longitudinal phonons LO are observed from surface (001) according to selection rule. Though for some compositions the transverse phonons TO were also fixed.

The system $Ga_{1-x}Al_xP$ was ascribed to the two-mode crystals.

With the method of excitation the Raman spectra of the films with various wavelengths of various lasers have been determined the thicknesses of films $Ga_{1-x}Al_xP$ on the basis of theoretical and experimental data. The thicknesses of films estimated by Raman scattering turned out to be in good agreement with estimations of thicknesses by microscope and electron probe.

Using various discrete wavelengths of exciting laser we have first found the resonance with the participation of the first direct zone E_0 for some films of $Ga_{1-x}Al_xP$.

The investigation carried out for this system is employed successfully for quantitative analysis of the same system synthesized by ion implantation.

In the seventh chapter one of the actual fundamental processes of Raman scattering, resonance Raman scattering (RRS), is studied. The RRS enables one to enhance the intensity of common Raman scattering by some order by means of selecting the corresponding exciting laser wavelength. This occurs when the wavelength energy of the exciting laser approaches to some electron transition energy of the object under investigation. In semiconductors such intermediate levels are indirect, direct zones, exciton and other electronic levels. The resonance occurring with the participation of each of the mentioned intermediate levels has its own theoretical ground and experimental manifestation. Thus RRS gives fundamental information about intermediate energy levels participating in resonance. Besides, its role in the field of analysis is great: it is possible to increase matter's detectability with its aid by some order. More over, there is variety of RRS increasing detectability even greater; it is now real to find single molecules by laser resonance Raman spectroscopy variety.

We have studied two types of resonance: the resonance in indirect zone semiconductors, GaP and α-HgS, occurring with indirect zone mechanism, and resonance Raman scattering occurring with direct exciton mechanism in direct-zone semiconductor mixed crystals $ZnTe_{1-x}Se_x$. We studied RRS for two compositions of these systems: $ZnTe_{0.6}Se_{0.4}$ and $ZnTe_{0.7}Se_{0.3}$.

The RRS of indirect zone semiconductors GaP and α-HgS has been studied by various discrete wavelength lasers and dye lasers. It turned out that if weak resonance in GaP is going with indirect zone participation, the resonance in the second indirect zone semiconductor cinnabar, α-HgS, is stronger. This fact is obvious from the experimental dispersion curves too. Such experimental fact we justify on the basis of the peculiarity of zone structure of cinnabar. This peculiarity becoming apparent in the RRS consists in the fact of existing the weak direct zone in cinnabar. Thus, we can suppose that in α-HgS the RRS occurs with intermediate mechanism to which besides indirect zone contributes the weak indistinct direct zone too.

RRS of classic direct zone semiconductors, $ZnTe_{0.7}Se_{0.3}$ and $ZnTe_{0.6}Se_{0.4}$, we studied with continuously working dye laser. The excitation of dye laser on dye Rodamin 6G occurred with integral radiation of argon laser.

RS spectra of solid solutions $ZnTe_{0.7}Se_{0.3}$ at various wavelength excitation of dye laser show that after using a certain magnitude of exciting wavelength (E=1.983 eV) in RS spectrum phonon 2LO appears, the intensity of which rises sharply when the exciting quantum energy approaches the forbidden gap width E=2.135 eV of $ZnTe_{0.7}Se_{0.3}$. Simultaneously the intensities of LO and TO phonons increase sharply. The phonon intensity increases by almost five orders. The analogous spectra were recorded in case of mixed semiconductor $ZnTe_{0.6}Se_{0.4}$.

The comparison of dispersion curves obtained by experimental data and theoretical calculations show clearly that just as in semiconductors of type A^2B^6, ZnTe, ZnSe, CdZnTe and in mixed crystals we have studied, in $ZnTe_{0.7}Se_{0.3}$ and $ZnTe_{0.6}Se_{0.4}$ also the RRS occurs with exciton mechanism.

In the eighth chapter semiconductor surfaces modified by ion implantation are studied by laser Raman spectroscopy. During implantation the crystal structure is destructing- the defects are formed. Defect formation may be so increased that after a certain critical limit the crystal changes into very disordered structure. The crystal structure transformation into disordered state depends on types of implanted ions and implantation conditions. Finally, the crystal may change into entirely amorphous phase.

Raman scattering is an important physical method for investigation of such phase transformations. But the main thing is that during Raman scattering study the object under investigation is not harmed.

By laser Raman spectroscopy we have studied structure changes caused by argon and boron ions implantation near surfaces (111) of GaP and GaAs.

Analyzing the Raman spectra showing processes of GaP and GaAs implantation with various doses of various ions we arrived at a conclusion that at various stages of ion implantation the above semiconductors undergo phase transformations. In various intervals of implantation doses we fixed due to Raman spectra crystalline, microcrystalline, nanocrystalline, amorphous and very disordered structures with partially broken bonds. Internal mechanical stresses, induced due to increase of volume of elementary cell because of implantation, are also to be taken into consideration. But this is equivalent to uniaxial stress effect on the crystal. From one's part this fact causes a little shift of phonon frequencies. A cluster mechanism of the mentioned phase transformation is suggested. Critical doses of amorphization of GaP and GaAs have been determined.

In the same chapter the questions of laser Raman spectroscopy identification and analysis of ternary semiconductors, $GaAs_xP_{1-x}$ and $Ga_xAl_{1-x}As$, synthesized near surface GaAs by phosphorous and aluminum ions implantation are discussed.

The technological conditions of synthesizing by ion implantation have been investigated; dynamical processes of distortion of long range ordering characterizing crystalline structure due to implantation and the dynamics of crystalline long range ordering recovering as a result of post thermal treatment have been studied. The substrate temperature role during ion synthesizing has been determined.