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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

MICROSTRUCTURE AND OPTICAL PROPERTIES OF THIN FILMS OF OPTOELECTRONIC MATERIALS Si, ZnO, CdS, $MoSe_2$, $InAs_{1-x}Sb_x$

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INTRODUCTION

State-of-the art and actuality of the topic. Increasingly speeding science progress, together with further miniaturization of electronic devices during recent decades has led to taking over new enough field of physics like microelectronics by more promising nanoelectronics. The transition down to the nanometer scale of the studied objects has produced a need for the use of the techniques capable of probing nanostructures and based on completely new principles. The operation of existing optical microscopes is significantly limited by a resolution of 200 nm, determined by the Rayleigh diffraction criterion.

A significant event for the development of the physics of low-dimensional systems and micro-objects was the creation, first of a scanning tunneling microscope (STM), and then an atomic force microscope (AFM) and various techniques based on them, which are currently united under a new direction of physical research - scanning probe microscopy (SPM). Today, scanning probe microscopy is one of the strongest modern methods for studying the morphology and local features of a solid object surface with a high spatial resolution of about 1 Angstrom.

The scanning probe microscope has become not only a research but also a technological tool during the recent years. It is successfully used to create new unique physical devices, such as a single-electron transistor, spin transistor, as well as for the manufacture of memory carriers with huge recording densities (up to 10^{10} bit / cm^2).

Scanning probe techniques are most widely used in studies of thin-film coatings. As we know, nowadays thin-film materials that have wide functional capabilities at small volumes, which, in its turn, contribute to the reduction in cost and miniaturization of the devices themselves, are widely used in optoelectronic devices.

Thin-film materials are made mainly by physical and chemical methods. In physical methods, the energy of particles of the substance falling on the substrate surface is much higher than in chemical ones, since deposition is performed in most cases in the magnetron discharge plasma (magnetron sputtering), molecular beams

(molecular beam epitaxy) or a laser torch (pulsed laser deposition). The high kinetic energy of particles gives an impetus to the formation of films with a more perfect crystal structure due to the high surface diffusion mobility of particles.

In the technology of obtaining high-quality thin films free from internal stresses and dislocations, an important role is played by the choice of a substrate on which the growth of thin films will happen. The obtaining of such microstructures is, in its turn a very unique and complex technological task, achieved by using special methods and modes of growing thin-film structures, the stress relaxation at which occurs mainly through the formation of imperfect dislocations located in the interface area.

The possibility of obtaining high-quality thin-film materials for the needs of modern optoelectronics (solar and thermoelectric converters, diode lasers, light emitting diodes, photodetectors, infrared imagers, saturable absorbers, modulators, filters, etc.), the emergence of new high-tech devices for diagnostics and comprehensive study of the physical properties of thin films stimulate more detailed research in this direction.

The functional load of a thin film in a device structure can be different. Depending on the required functionality (required design), the film production technology (technological design) can vary and include, besides the main production method, additional alloying and even surface modification of the already obtained film. The ideal design and final production technology are established by using different production methods and additional procedures until the required functionality is achieved, which, in its turn, is verified by purely physical methods.

The given work is devoted to the post-technological analysis of physical phenomena in thin films of Si, ZnO, CdS, $MoSe_2$ and $InAs_{1-x}Sb_x$, the design of which implies a detailed consideration of their microstructure, optical, and, in some cases, electrical properties.

The purpose and objectives of the research. The purpose of the dissertation is to study the microstructure, optical and, in some cases, electrical properties of thin films of commercial semiconductor

materials Si, ZnO, CdS, $MoSe_2$ and $InAs_{1-x}Sb_x$, with different, depending on the material, technological design of a thin film.

In order to achieve this purpose, the objectives of total post-technological characterization of the structure, morphology, optical, and in some cases, electrical properties of thin films with the following technological design for each of the mentioned materials were set and solved:

1. Standard commercial silicon structure Si: B / SiO_2 (buried buffer silicon oxide layer) / Si: B (substrate) and the same structure with a subwavelength diffraction grating obtained by nanograting the surface of a thin Si: B layer with the aid of laser lithography method.
2. Fullerene C_{60}/Si and fullerene C_{60}/ porous Si thin-film structures.
3. Thin-film structures ZnO / substrate and ZnO: Al / substrate obtained by magnetron sputtering on soda lime glass substrates in an oxygen / argon gas mixture atmosphere with different O / Ar ratios (0-6% O_2).
4. Obtained on a glass substrate by aerosol pyrolysis method from solutions with different pH values thin-film pattern of CdS / substrate with a nanostructured thin film of CdS.
5. Non-relaxed heteroepitaxial structures $InAs_{1-x}Sb_x$ at x = 0.43 and 0.38, obtained by molecular beam epitaxy method with the ideal choice of an intermediate buffer of variable composition for a smooth change in the lattice parameter and the selection of optimal thicknesses and modes (temperature and time) of epitaxial growth of buffer and working layers.
6. Thin-film structure $MoSe_2$ / substrate obtained by magnetron sputtering of Mo onto a glass substrate and subsequent thermal processing of the gained film in saturated vapors of selenium.

Research methods. The main sources for obtaining data on microstructures in this work were:

−Scanning Probe Microscopy (SPM) - atomic force (AFM) and tunnel (STM),

− Scanning electron microscopy (SEM), including elemental analysis (EDXS – Energy Dispersive X-ray Spectroscopy)

−Transmission electron microscopy (TEM) and

−X-ray diffractometry.

The methods for studying the optical properties were:

−Spectroscopic ellipsometry, that gives complete information about the dielectric function, which describes all optical properties of the material with the exception of luminescence and Raman scattering,

− Standard and confocal photoluminescence spectroscopy,

− Confocal Raman scattering microscopy.

Basic scientific theses put forward to defend. Fundamental rearrangement of the electronic spectrum of silicon and a giant increase in conductivity at the interface of a thin silicon layer / buffer silicon oxide layer are resulting from the grated surface with a period comparable to the De Broglie wavelength of electrons near the Fermi level.

- An intensity growth by two orders of magnitude and domination of the molecular radiative transitions over the interband transitions in the solid-state fullerene C_{60} / porous silicon / silicon structure in comparison with the structures containing this fullerene on glass or silicon are associated with deep penetration of monomolecular C_{60} into the pores of silicon and relaxation of selection rules for optical transitions due to the strong interaction of the permeated molecules with the walls of pores.
- Spectral features of the photoluminescence of thin CdS films in the presence of crystalline grains with sizes less than 10 nm in the matrix are a consequence of the quantum size effect.
- A low concentration of nanosized (<10 nm) CdS particles, as radiation centers with a huge oscillator strength, but a negligible density of states in comparison with the density of eigenstates of bulk CdS leads to the difficulty of detecting the quantum size effect in the CdS dielectric function.
- Within Bruggeman effective medium approximation, the parameter describing the optical degree of crystallinity of a thin film is found analytically.

- Coherent growth of $InAs_{0.57}Sb_{0.43}$ and $InAs_{0.62}Sb_{0.38}$ solid solutions on AlGaInSb and GaInSb gradient buffer layers, respectively, is due to the localization of mismatch defects at the substrate-buffer interfaces and a low density of threading dislocations (less than 10^7 per cm^2).
- The imaginary part of the dielectric function of $MoSe_2$, retrieved experimentally by spectral ellipsometry method and calculated using the density functional, is qualitatively in a good agreement in a wide range of photon energies, except for the range of the optical transitions near the energy gap, due to neglecting Coulomb interaction of an electron and a hole in the framework of the one-electron approach.

Scientific novelty of the research.

1. It is shown that nanograting (with a period less than 250 nm) at the interface between thin silicon layer and silicon oxide buffer layer leads to the formation of a surface superlattice with characteristic radiative transitions inherent in a quantum well.
2. It is shown that in silicon structures with a subwavelength diffraction grating, there is a significant increase (by 2-3 orders of magnitude) in the concentration of free electrons.
3. It is shown that thin film of C_{60} fullerene on a glass substrate is a mixed system molecular crystal - band semiconductor, with characteristic radiative transitions between vibronic states of the Frenkel singlet exciton, on the one side, and radiative interband transitions at the fundamental absorption edge on the other side.
4. It is shown that, at least for films of wide-gap semiconductors (such as, for example, ZnO), it is necessary to introduce the optical degree of crystallinity, which shows how much the values of dielectric function of the film differ from those for an ideal monocrystal.
5. It is shown that a change in the composition of thin films of the $InAs_{1-x}Sb_x$ solid solution, making it possible to reduce the band gap down to 100 meV, does not lead to an increase in the defectiveness and violation of the high degree of homogeneity inherent in InAs and InSb.

Theoretical and practical significance of the research.

Theoretical significance of the research is related to the physics developed within the frames of the existing concepts about interaction between electromagnetic radiation and matter in order to describe the complicated optical phenomena observed on the subwavelength surface diffraction grating with a period comparable with De Broglie wavelength of the electron in crystal and in the case of a mixed semiconductor-molecular crystal system.

The results of studies of silicon structures with a subwavelength diffraction grating obtained in this dissertation are the first step in the development of quantum well lasers with a wavelength controlled by the period of the diffraction grating. In addition, nano-grating can be used for electronic doping of semiconductor materials without chemical introduction of impurities (the so-called G-doping).

Data from studies of thin films of ZnO, ZnO: Al and CdS can be useful for creating a wide-gap window layer in the framework of TCO (Transparent Conductive Oxide) technologies in designing second-generation solar cells.

Such a universal parameter as the optical degree of crystallinity, introduced in this work, can serve for express analysis and accurate assessment of the quality of an optoelectronic material obtained as a result of a particular technological process.

The results of the researches of non-relaxed hetero-epitaxial structures $InAs_{1-x}Sb_x$ at x = 0.43 and 0.38 can be used to develop and create diode lasers, light-emitting diodes (LEDs), photodetectors, etc. in the technologically important spectral region from 3 to 12 μm, into which the windows of transparency of the atmosphere fall.

Data on the microstructure and optical parameters of thin-film structures, including $MoSe_2$, can be used in the design and creation of miniature and low-cost phototransistors and sensors.

Personal contribution of the author. The author solely conducted the studies and analysis of the microstructure of thin films, participated directly in optical experiments, individually treated the obtained data with the aid of the specialized program resources and conducted the joint analysis of the obtained results, as a whole, using modern concepts about the interrelation between the structure and physical processes in semiconductors and molecular crystals under

the impact of electromagnetic radiation.

Approbation and application. The results of the research presented in the dissertation were discussed at International conferences International Conference Thin Films ICTF 16, (Croatia, Dubrovnik, 2014), Baku World Forum of Young Scientists (Azerbaijan, Baku, 2014), International Conference on Ternary and Multinary Compounds ICTMC 19 (Japan, Niigata, 2014), Materials Science and Engineering MSE 2014 (Germany, Darmstadt, 2014), International Conference on Spectroscopic Ellipsometry ICSE-7 (Germany, Berlin, 2016), ICTMC 20 (Germany, Halle, 2016), XIV International Conference « Physics of dielectrics » (Russia, St.Peterburg, 2017), 17 International Workshop on New Approaches to High-Tech: Nano-Design, Technology, Computer Simulations (Belarus, Minsk, 2017), 25 Annual International Conference on COMPOSITES/NANO ENGINEERING ICCE-25 (Italy, Rome, 2017), 52nd School of the Federal State Budgetary Institution "PNPI" on Condensed Matter Physics (Russia, St. Petersburg, 2018).

The developed method of scribing using AFM to obtain diffraction gratings with a period of 100 nm on the surface of semiconductors, which is still unattainable for existing industrial technologies, is an important nanotechnological process that brings the grating period closer to the De Broglie wavelength of electrons in semiconductors and opens the way to the use of quantum effects in commercial materials at room temperature. The developed method is patented (Patent: "Method for the formation of nanoscale elements on a thin layer of semiconductor material" i 2016 0086)

The name of the organization in which the dissertation work is completed. The dissertation work is completed at the Innovation Sector of the Institute of Physics of the Azerbaijan National Academy of Sciences.

Published works. The main materials of the dissertation were published in 28 publications, of which 15 articles (also 9 in foreign journals with an impact factor) and 13 theses.

Volume, structure and main content of the dissertation.

The dissertation consists of an introduction (8 pages), five chapters (I chapter 18 pages (17275), II chapter 44 pages (49261), III

chapter 24 pages (22723), IV chapter 36 pages (32804), V chapter 28 pages (22323)) conclusions (2 pages (2938)), set out on 176 pages, including 68 figures, 6 tables and a list of cited literature of 115 titles.

THE CONTENT OF THE WORK

The introduction validates the relevance of the chosen topic, formulates the purpose and main objectives of the work, scientific novelty, practical significance of the work, gives the main provisions for defense, and summarizes the main content of the dissertation.

The first chapter «Research methods for investigation of crystal structure and morphology of bulk and thin-film materials» of the dissertation describes in detail the structure and principle of operation of an atomic force microscope and a scanning tunneling microscope. The modes of operation of atomic force and tunneling microscopes are given. The accuracy of measurements and factors affecting the sensitivity and spatial resolution of devices are given.

There are various methods for studying the structure of the crystal structure of bulk and thin-film materials. These are methods of diffraction of X-rays, neutrons (neutron diffraction) and electrons (electron diffraction).

In order to study the structure of crystals, we mainly used high-resolution X-ray diffraction method. And to determine the correspondence between the parameters of thin-film structure grid and the substrate, the rocking curves were recorded and the reciprocal space maps were studied.

To study the morphology and local features of the surface of bulk and thin-film materials with high spatial resolution, we used modern methods of scanning probe microscopy of surfaces - atomic force microscopy, tunnel microscopy and scanning electron microscopy.

X-ray diffraction studies of the obtained thin-film structures were carried out on an X-ray diffractometer Bruker D8 Advance

Bruker comp., Germany and on an X-ray diffractometer Bruker D2 Phaser, Bruker comp., Germany.

With the help of a Bruker D8 Advance X-ray diffractometer, it is possible to carry out:

1. qualitative and quantitative analysis of crystalline phases,
2. determination of crystallite sizes,

Scanning probe microscopy (SPM) is one of the strongest modern methods for studying the morphology and local properties of a solid surface with high spatial resolution. In our studies, we used an AIST-NT microscope (Tokyo Instruments, Japan) operating in the modes of atomic force and tunneling microscopes.

The working part of such probes (tip) has dimensions on the order of nanometers. The characteristic distance between the probe and the surface of the samples in probe microscopes in order of magnitude is 0.1 - 10 nm.

The second chapter «Silicon structures with subwavelength diffraction grating and fullerene (C_{60}) layer on the surface» gives the results on the study of the electrical and optical properties of a nano-grated Si layer obtained on the surface of the Si / SiO_2 device structure, as well as the optical properties of thin films of C_{60} fullerene deposited on the surface of porous silicon (PS). Studies of the electrical features were conducted by the 4-probe method.

A noticeable metallization of the nanograted Si / SiO_2 structure was found, which is explained by an increase in the number of conduction electrons due to the depression of occupied quantum states in the valence band of silicon.

It is necessary to mention that, the aforementioned increase in the concentration of conduction electrons or the so-called geometrically induced doping (G-doping) is the result of rearrangement of the spectrum of electrons` eigenstates. The effect of G-doping was also found on optical transitions in the regions above the energy gap of the semiconductor layer with a surface lattice. In particular, in nanograted structures in the photon energy range of 1.1–3.2 eV, at which interband optical transitions in Si are forbidden, a broad and intense emission is observed with partially resolved and almost equidistant peaks separated by ~ 130 meV.

The possibility of nano-heating material surface with the help of an atomic force microscope is demonstrated, in case the hardness of this material is at least an order of magnitude lower than the hardness of the cantilever tip.

C_{60} / glass, C_{60} / Si, C_{60} /porous Si (PS)/ Si, as well as PS / Si structures for comparison, were investigated by photoluminescence spectroscopy at room temperature. Along with broadband low-energy radiation at 1.774 eV in the photon energy range of nominally forbidden optical transitions, C60 films on a glass substrate exhibit high-energy emissions at 2.115 eV and 2.342 eV in the range of allowed dipole transitions. On the other hand, C_{60} films on Si or PS / Si show only a 1.774 eV emission band. The intensity of this radiation in C_{60} / PS / Si is 200 times higher than in C_{60} / Si, and at least 20 times the intensity of radiation observed on porous Si / Si. Such a sharp increase in the radiation intensity indicates a weakening of the selection rules for nominally forbidden optical transitions and suggests a strong interaction of C_{60} molecules with porous silicon walls. The molecular signatures of C_{60} films are obviously shown in vibronic transitions with an energy separation of 60 meV (Ag mode energy) between the emission levels observed in the 1.774 eV emission band in C_{60} / PS / Si. The origin of the 2.115 and 2.342 eV emission bands is analyzed in terms of the band structure of a standard semiconductor, as well as the obtained ellipsometric data. The first corresponds to interband transitions between the bottom of the conduction band and the top of the valence band. The appearance of the second is apparently associated with the splitting of the valence band at the X point of the Brillouin zone of the C60 film due to the intra-crystalline field, and the magnitude of the splitting by the crystal field is ~ 200 meV.

The third chapter «ZnO and CdS thin films for application in efficient solar convertors» describes the technology for producing thin films of ZnO, ZnO: Al and CdS, comprehensive studies of their physical properties

ZnO and ZnO thin films: Al were deposited on soda lime glass substrates by magnetron sputtering at substrate temperatures of 200–400 ° C in an oxygen / argon gas mixture with different O / Ar ratios

(0–6% O_2). Higher degrees of crystallinity for ZnO: Al and ZnO films were achieved at a substrate temperature of 400 ° C and at a (O / Ar) mixture ratio of 0% and 4%, respectively. The crystallinity of films deposited at a temperature of 300 ° C demonstrates relatively low values and has a maximum at 2% O2.

AFM studies of the surface of ZnO films revealed that the surface is irregular with some voids, but it improves at a 4% O / Ar ratio, which correlates with the data on the crystallinity of the films from X-ray diffraction studies.

Based on the data of spectral ellipsometric studies, it was revealed that the structures in the dielectric function (both in its real (εi) and imaginary (εr) parts) of ZnO: Al films deposited at ratios of 2-4% O / Ar broaden and shift to the region lower energies, which indicates a high concentration of defects in these samples. In ZnO films, the minimum broadening of the dielectric function occurs at an oxygen concentration of 4%, and the position of the peak absorption is stabilized at 3.29 eV.

Analysis of AFM and X-ray data for ZnO: Al and ZnO, on the one hand, and data on the dielectric function, on the other, shows that a strong correlation between these data is not always observed, especially if we take into account the fact that the broadening of the imaginary part of the dielectric function, is known to be inversely proportional to the grain size. Therefore, it is advisable to use an optical degree of crystallinity, which shows how much the dielectric function differs from that for an ideal single crystal.

Let ε_i be imaginary part of the dielectric function ε, иmeasured on a polycrystalline film, ε_i^c is the supposed part of the reference dielectric function ε^c, measured on a single crystal, ε_i^a is a supposed part of hypothetical dielectric function ε^a for amorphous material. Then, by definition of the degree of crystallinity: $\varepsilon_i = f\varepsilon_i^c + (1 - f)\varepsilon_i^a$, where f is the degree of crystallinity. On the other hand, in the

BEMA[1] (Bruggeman Effective Medium Approximation) approximation, we have:

$$f\frac{\varepsilon^c-\varepsilon}{\varepsilon^c-2\varepsilon}+(1-f)\frac{\varepsilon^a-\varepsilon}{\varepsilon^a-2\varepsilon}=0$$

The complex equation for determining the degree of crystallinity then has the following form:

$$1+\frac{2}{\pi}\int_0^\infty \omega'\frac{\varepsilon_i(\omega')-f\varepsilon_i^c(\omega')}{1-f}\frac{}{(\omega')^2-\omega^2}\,d\omega'+i\frac{\varepsilon_i(\omega)-f\varepsilon_i^c(\omega)}{1-f}$$
$$=Re\left(\frac{\varepsilon(\omega)\varepsilon^c(\omega)+2\varepsilon(\omega)^2-3f\varepsilon(\omega)\varepsilon^c(\omega)}{\varepsilon^c(\omega)+2\varepsilon(\omega)-3f\varepsilon(\omega)}\right)$$
$$+Im\left(\frac{\varepsilon(\omega)\varepsilon^c(\omega)+2\varepsilon(\omega)^2-3f\varepsilon(\omega)\varepsilon^c(\omega)}{\varepsilon^c(\omega)+2\varepsilon(\omega)-3f\varepsilon(\omega)}\right)$$

and contains two equations (one for the real part, one for the imaginary) and the degree of crystallinity *f*, as unknown. For this reason, it is enough to equate the left and right imaginary parts of this equation, obtaining a cubic equation for *f*. The solution to this equation in an analytical form is known. There are three possible options: a) the solution has one real and two supposed roots, b) the solution has two real and one supposed root, and c) all three roots are real and different from each other. In each of these cases, a real positive root is chosen in the interval $0 \div 1$

The studies of the electrical conductivity of ZnO and ZnO: Al films have been carried out. The conductivity of the film obtained at 400 ° C in an atmosphere of pure Ar is 3.5×10^2 Ohm^{-1} cm^{-1} and decreases with an increase in the oxygen content in the O / Ar mixture. The decrease in conductivity with an increase in the oxygen content in the ZnO: Al film deposited at a temperature of 400 ºC can be explained by the formation of Zn vacancies, which, in the case of an excess of oxygen, are acceptor defects in ZnO.

[1] Adachi, S. Optical Properties of Crystalline and Amorphous Semiconductors: Materials and Fundamental Principles / – Springer Science, –1999. – 271 p. p.120–124.

At the end of the chapter, a technique for producing thin CdS films is described. The grain size of thin CdS films deposited by conventional pyrolysis decreases with an increase in the pH of the reaction solution. The photoluminescence (PL) spectrum of a film deposited from a solution with pH = 10.2 shows broadband emission located at 460 nm (2.7 eV), which can be explained by the quantum size effect at grain sizes <10 nm. No changes in the dielectric function due to the quantum size effect are observed, which is caused by a low concentration of nanosized (<10 nm) CdS grains, as emission centers with a huge oscillator strength, but a negligible density of states compared to the density of eigenstates of bulk CdS.

The fourth chapter «Unrelaxed heteroepitaxial structures $InAs_{1-x}Sb_x$ (x=0.43, 0.38)» shows data on the technology of obtaining unrelaxed heteroepitaxial structures $InA_{s1-x}Sb_x$ and their studies by various physical methods.

From studies of X-ray diffraction of various compositions of solid solutions «ZnO and CdS thin films for application in efficient solar convertors» was identified that, with a decrease in the number of antimony Sb atoms in the composition of the solid solution, along with a change in the intensity of the reflections, the position of the peaks of the reflections is shifted towards larger angles, which indicates a decrease in the lattice constant. Indeed, antimony atoms, in comparison with arsenium atoms, have a large radius, and with a decrease in their relative amount in a solid solution, it is natural to expect a decrease in the lattice constant. This is also consistent with the implementation of Vegard's rule.

A joint analysis of the experimental data obtained by high-resolution X-ray and electron microscopy methods showed that the obtained solid solutions $InAs_{0.57}Sb_{0.43}$ and $InAs_{0.62}Sb_{0.38}$ grow coherently on gradient buffer layers AlGaInSb and GaInSb, respectively.

The obtained heteroepitaxial structures have good structural quality, which can be traced from the shape of symmetric and asymmetric reflections in reciprocal space.

Transmission electron microscopy data indicate that the upper layers of the heteroepitaxial structure $InAs_{1-x}Sb_x$ are unrelaxed and

unstressed, and dislocations in them are mainly localized near the interface.

Atomic force microscopy studies of surface morphology revealed a high degree of surface quality for the obtained heteroepitaxial structures. The roughness of the film, determined by the value of RMS (Root Mean Squared), turned out to be less for films $InAs_{0.57}Sb_{0.43}$, deposited on the intermediate buffer AlGaInSb than for $InAs_{0.62}Sb_{0.38}$ on the buffer GaInSb: for $InAs_{0.57}Sb_{0.43}$ – 4.3 nm, for $InAs_{0.62}Sb_{0.38}$ – 5.8 nm.

With energy dispersive X-ray spectroscopy method (EDX or EDS) elemental analysis of the heteroepitaxial structure $InAs_{1-x}Sb_x$ with high spatial resolution was carried out. The resolution of the EMF analysis depends on the thickness of the sample, the accelerating voltage and the diameter of the electron probe and reached 0.2 nm. From an analysis of the elemental composition of the epitaxial heterostructure in depth, it was shown that, as it should be, the surface contains mainly the elements In, As, and Sb; in the middle, in the region of the intermediate buffer, elements Ga and Al appear, the content of which actively changes, and when approaching the substrate is dominated by the concentration of elements Ga and Sb.

The data of studies of Raman scattering of light in heteroepitaxial structures $InAs_{1-x}Sb_x$ are presented in detail. It is known that in bulk InAs single crystals the frequency of the longitudinal LO phonon is 242 cm^{-1}, and that of TO is 220 cm^{-1}, in InSb the frequency of the LO phonon is 193 cm – 1, and that of TO is 185 cm^{-1}. We observed several phonon bands. This is an intense phonon band at frequencies allowed by the selection rules for a given scattering geometry is 187 cm^{-1} ($InAs_{0.57}Sb_{0.43}$) and 186 cm^{-1} ($InAs_{0,62}Sb_{0,38}$) corresponding to a longitudinal optical phonon in InSb (InSb-like LO) and an asymmetric wide phonon band at frequencies 222 cm^{-1} ($InAs_{0.57}Sb_{0.43}$) and 223 cm^{-1} ($InAs_{0,62}Sb_{0,38}$), representing the superposition of two bands from optical longitudinal and transverse phonons in InAs (InAs-like LO and InAs-like TO). It is seen that as the number of Sb atoms decreases in $InAs_{1-x}Sb_x$ (sample $InAs_{0,62}Sb_{0,38}$) the frequency 222 cm^{-1} shifts towards higher frequencies, i.e. Raman frequencies of active phonons characteristic

of InAs. Confocal Raman spectroscopy (RS) data indicate a two-mode type of rearrangement of phonon spectra in solid solutions $InAs_{1-x}Sb_x$.

The high homogeneity of the obtained heteroepitaxial structures is confirmed by the data of studies of the micro-Raman spectra by scanning a laser beam over the surface of the structure (with an area of 50 μm × 50 μm) in the mapping mode. This chapter summarizes the results of mapping the peak position and half-width of spectral lines 187 cm^{-1} and 222 cm^{-1}.

Spectral ellipsometric studies of heteroepitaxial structures $InAs_{1-x}Sb_x$. The real ε_i and supposed ε_r parts of the dielectric function $InAs_{0.57}Sb_{0.43}$ and $InAs_{0.62}Sb_{0.38}$ for different photon energies were determined. A similar nature of the dependences was noted, which is not surprising for compounds with such a similar structure and similar compositions. There is a good correlation of features on the dependencies $\varepsilon_r(E)$ and $\varepsilon_i(E)$ with parent compositions InAs and InSb. The dispersion dependences of the refractive indices n(E) and extinction k(E) for the film $InAs_{0.57}Sb_{0.43}$ are calculated and plotted.

The fifth chapter «Structure and optical properties of $MoSe_2$ thin films» provides data on the technology of obtaining thin films of $MoSe_2$, their characterization by X-ray diffraction and Raman scattering of light, and studies of the optical properties by the method of spectral ellipsometry and theoretical calculations of the electronic band structure.

$MoSe_2$ layers less than 100 nm thick were obtained by annealing molybdenum films in saturated selenium vapor. The crystal structure was studied by X-ray diffraction and lattice dynamics by Raman light scattering. Spectral lines of Raman-active optical phonons E_{1g} (167.5 cm^{-1}), A_{1g} (241 cm^{-1}) and $E_{2g}{}^1$ (286 cm^{-1}). characteristic of $MoSe_2$ have been revealed. On an area of 1 × 1 μm, the AFM method was used to study the surface morphology of $MoSe_2$ thin films and the average crystallite size of about 10-50 nm was determined.

The method of spectroscopic ellipsometry was used to study $MoSe_2$ thin films and a polycrystalline $MoSe_2$ target in the ultraviolet / visible / near infrared spectral range. The experimental data were processed within the optical dispersion model described by the B-

spline procedure (this procedure is available in the database of the Complete Ease software package), and dielectric functions were obtained for both the thin layer and the target. It turned out that the best fit was obtained when the dielectric function of $MoSe_2$ was taken in a mixture with the dielectric function of pure selenium. In the approximation of the already mentioned Bruggemann effective medium approximation, the required amount of selenium was 16 percent.

The presence of pure selenium is obvious, since the measurements were carried out on prepared samples without annealing them in vacuum. The mean squared error (MSE) of the fit for all three angles of incidence was simultaneously lower than 11.4. The selected optical model was used to determine the dispersion of the complex dielectric function of the $MoSe_2$ layers and to calculate the dispersion of the refractive indices n and extinction k (real and supposed parts, ε_i and ε_r).

The band structure of $MoSe_2$ was calculated using the WEIN2k software package based on the density functional theory (DFT) and full-potential linearized augmented plane waves. The exchange correlation effects are described in the LDA-local density approximation. In the visible region, the imaginary part of the dielectric function is calculated using the combined density of states. Integration over the Brillouin zone was carried out by the Monkhorst-Pack method. The real part of the dielectric function is obtained using the Kramers-Croning relation. The obtained dielectric function turned out to be in good agreement with the dielectric function obtained from the analysis of ellipsometric data on a $MoSe_2$ target in the energy range above 1 eV. The observed feature of the imaginary part of the dielectric function of about 1 eV is assumed to be associated with indirect exciton transitions.

CONCLUSIONS

1. The microstructure of thin films of commercial semiconductor materials Si, ZnO, CdS, $MoSe_2$ and $InAs_{1-x}Sb_x$, with different,

depending on the material, technological design of the thin film was determined by scanning probe microscopy.

2. The method of measuring electrical conductivity revealed a giant increase (by 2-3 orders of magnitude) in the concentration of free electrons in silicon structures with a nano-grated surface in comparison with the case of a flat surface of a thin surface layer of silicon.
3. Nanograting leads to the appearance of a new critical point in the interband density of states for optical transitions and broadband photoluminescence with equidistant peaks, the energy position of which depends on the excitation wavelength and corresponds to the region of forbidden transitions in standard silicon.
4. Optical transitions above 2 eV, which form the dielectric function of a thin film of C_{60} fullerene deposited on a glass substrate, are well described by the model of a standard direct-gap semiconductor with a band gap energy of 2.115 eV and a crystal-field splitting energy of ~ 200 meV at room temperature.
5. The sharp increase in the radiation intensity in the C_{60} / PS / Si structures in comparison with the C_{60} / glass and C_{60} / Si structures is a consequence of the relaxation in porous silicon of the selection rules for transitions forbidden in the case of ordinary silicon.
6. According to the obtained microstructural data, higher degrees of crystallinity of thin ZnO: Al and ZnO films obtained by magnetron sputtering are achieved at a substrate temperature of 400 ° C and a (O / Ar) mixture ratio of 0% and 4%, respectively.
7. According to the obtained microstructural data, the grain size of thin CdS films deposited by the conventional pyrolysis method decreases with an increase in the pH of the reaction solution. The photoluminescence spectrum of a film deposited from a solution with pH = 10.2 shows a broad emission band located at 460 nm (2.7 eV), which can be explained by the quantum size effect at grain sizes <10 nm.
8. High-resolution X-ray diffraction, atomic force and transmission electron microscopy revealed that solid solutions

$InAs_{0.57}Sb_{0.43}$ and $InAs_{0.62}Sb_{0.38}$ grow coherently on the gradient buffer layers AlGaInSb and GaInSb, respectively, and misfit defects are localized at the substrate-buffer interfaces, and the density of threading dislocations is less than 10^7 cm^{-2}.

9. Confocal Raman microscopy of epislodes of solid solution $InAs_{1-x}Sb_x$ confirms the two-mode nature of the behavior of phonon modes and a high degree of homogeneity of compositions with x = 0.43 and 0.38.
10. The observed feature near 1 eV in the imaginary part of the dielectric function of $MoSe_2$ thin films is due to indirect exciton transitions. Far from this feature, the experimental data on the dielectric function are in good agreement with those calculated within the one-electron approximation with the use of the density functional.

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