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SINGLE-CRYSTALLINE SUPERIONIC CONDUCTORS WITH FAST PROTON TRANSPORT

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Materials in which fast ion transport with low activation energy can occur are termed superionic conductors. In the superionic phase the number of sites available for the ions should be greater than the number of the ions, the energetic barriers between the equilibrium ion sites should be low and the structure should allow a free path for the ions. The behaviour of protons as charge carriers in solid is different than that of the other ions and in the case of fast proton transport the migration of protons has to be correlated with the dynamics of their surroundings. Fast structure diffusion of protons in the superionic phase of hydrogen sulphates resides in proton transfer between the XO_4 tetrahedra and subsequent reorganization of the proton environment and moreover, the anisotropy of the protonic conductivity is determined by the structural conditions.

Phase transitions in proton containing crystals are often related to the proton ordering in the hydrogen bonds. A variety of proton ordering appears in the low-temperature phases of hydrogen sulphates and selenates:

1. zig-zag chains of asymmetric XO_4 tetrahedra liked with short hydrogen bonds are characteristic of $MeHXO_4$
2. isolated O_3XO-H...OXO_3 dimers appear in crystals of $Me_3H(XO_4)_2$ family
3. three XO4 tetrahedra linked with short hydrogen bonds form trimers in the structure of a $Me_4H_2(XO_4)_3$ type crystal
4. structural motif of $Me_4LiH_3(XO_4)_4$ crystals consists of four XO_4 tetrahedra linked with hydrogen bonds in the form of folded tetramers.

The behaviour of fast proton transport in crystals exhibiting various types of proton ordering will be discussed and structural aspects of fast proton transport in $(NH_4)_3H(SeO_4)_2$ will be presented [1,2].

The phase with fast proton transport in hydrogen sulphates and selenates is characterized by high structural disorder consisting in a translational disorder of the protons in hydrogen bonds, an orientational disorder of the XO_4 tetrahedra and, in ammoniumcontaining crystals, in an orientational disorder of NH_4. When the crystal is cooled down from the highly disordered superprotonic phase to the low-temperature phase both the molecular structure (chains, dimers, trimers, tetramers) and the crystallographic structure have to be recovered. Results of our NIR Raman and protonic conductivity studies of the recovery processes in $(NH_4)_4H_2(SeO_4)_3$ will be presented [3-5].

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HOW CRYSTAL GROWTH BECAME IN THE LAST 75 YEARS A SCIENTIFIC PLURIDISCIPLINARY FIELD

R. Kern
Former President of IOCG, France

Crystal growth started in the 20th as isolated works in the field of physical-chemistry with the theoretical works of Kossel, Stranski, Volmer and other outstanding scientists. Only before and during world-war II the technical side of growing single crystals was developed. In the early 50th this effort boosted again fundamental and theoritical studies with the trio Burton, Cabrera, Frank well known scientists in other fields. Up to that time there was only observation of crystals to support theory, no real experimentation was done. Interaction between theory and planed experimentation came only in the 60th. The result was an exponential increase of activity overall the world. At the same time started also the idea to use crystals as electronic devices. It is difficult to say who was boosting the other. Good crystals were needed by industry, industry asked to produce better ones. This deal was only possible by the interaction of fundamental research in crystal growth and technical preparation of single crystals. Also the field became connected to material science, a new field where new materials of given properties are produced. Some of such materials had to be prepared as single crystal. An exact description where crystal growth activities are crucial would be a too long story. Only an enumeration could be easy to do. One point is sure: for covering so many different crystal growth activities the field needs to be pluridisciplinary. The classical scientific societies, groups or associations could not fullfil this condition. Therefore in the 65th specific conferences started to be organized, International Conference of Crystal Growth took place in Boston and was called number 1. This year in Kyoto number 13 will take place. During these 40 years most countries organized themself by creating their national organisation of crystal growth, to the great benefit of the national scientific production. Sometimes this was easy, sometimes less easy depending on the resistance the traditional national associations offered.

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SCIENCE OF CRYSTAL GROWTH APPLIED TO COMPLICATED SYSTEMS

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During the 20th century, we reached a state that we understand at atomic or molecular level how crystals nucleate, grow, and their morphology, perfection and homogeneity are controlled at least for simple and mono-component systems. This has enabled us to utilize structure-sensitive properties of crystalline materials efficiently in our daily life, in form of devices obtained either from bulk single crystals or thin films whose perfection and homogeneity are well controlled. However, we still have not reached this state in understanding growth related phenomena in complicated and complex systems. For such systems, we may mention the followings; texture formation in ceramics, formation of minerals in solid earth and planetary materials, including cosmic dusts and silicate and organic meteorites, biomineralization and origin of life. These problems have been investigated mainly on equilibrium thermodynamic consideration. If the problems could be understood on the basis of kinetic processes, this will give a new light to respective fields. We may also expect to open new industries, by controlling texture formation in complicated and complex systems. Based on our understanding on atomic process of crystal growth achieved during the 20th century, this should be possible. It will also give us an enjoyment of decoding a detective story The author considers this will be an important research target of science of crystal growth in the 21st century. The presentation will start with recollecting how the authors were interested in the science of crystal growth, morphology, surface microtopography, perfection and homogeneity of mineral crystals. This will be followed by a case study of decoding a letter sent from the depth of the earth, taking natural diamond crystals as a representative example.

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CRYSTAL GROWTH AND PHASE TRANSITIONS

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In growing single crystals, on is primarily concerned with obtaining a crystal of predetermined size with a high degree of structural perfection and a well-determined chemical composition.

Growth of a single crystal requires the nucleation, subsequent growth, eventual termination of the process and, finally, removal of the crystal from the apparatus. Each step of the growth process is affected by controlling the experimental parameters pressure, temperature, and concentration.

Crystal growth for the melt, from solution and from the vapor phase is determined by phase transitions of first order characterized by a congruent or an incongruent behaviour. For this reason the investigation or knowledge of (p-)T-x-phase diagrams is absolutely necessary, and the main types of phase diagrams corresponding to crystal growth will be presented and discussed.

Furthermore, one or several solid-solid phase transitions of first or second order between the growth temperature and room temperature can dramatically influence the structural quality of the as-grown crystals. A short overview about the types of solid-solid phase transitions will be also given.

A lot of materials with solid-solid phase transitions are of considerable interest for basic research or application and the growth and cooling strategy will be presented in the case of the perowskite $KNbO_3$ *(m3m→4mm→mm2)*, the tetragonal tungsten bronze $K_6Li_4Nb_{10}O_{30}$ (KLN) *(4/m mm→4mm)* and the ferroelastic $Pb_3(PO_4)_2$ *($\bar{3}$ m→2/m)*.

$KNbO_3$ single crystals have been grown by the top seeded solution growth (TSSG) method and the domain structure was analysed by high resolution X-ray diffractometry. From twelve possible domains six can be detected by X-ray methods. However, at the investigated as-grown crystal only two different domains were found with one common a-axis. It is suggested that the restricted observed domain pattern is closely related to the crystal growth and cooling processes, both influenced by the seed crystal.

In the case of KLN only one ferroelectric phase transtion occurs at about 480°C. Problems with this phase transition are correlated to cracking and can be overcome by choosing a convenient melt composition and seed orientation.

The nature of solid-solid phase transitions of first order in solid solution systems like $Pb_3(P_{1-x}V_xO_4)_2$ and $KNb_{1-x}Ta_xO_3$ was investigated by means of DSC and polarising microscopy.

In a special temperature cell a nearly linear temperature gradient could be realised over the samples, being capable of observation the phase transition between crossed polars. The solid-solid phase boundary is sharp in the case of the compound and diffuse in the case of the mixed composition. A model assuming also a "liquidus line" and "solidus line" in the solid state described by the van-Laar equation will be presented.

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ROLE OF GAS PHASE IN THE GROWTH OF SOME OXIDES BY THE CZOCHRALSKI METHOD

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The Czochralski method is universally accepted for the crystallization of a variety of compounds used in the electronics technology. Mono- and polycomponent oxides belong to a group of compounds which are widely used in nonlinear optics, in dielectric applications and as substrates in the thin film technology. Some crystals are almost free of volume defects but point defects appear in them as F-centers. These color centers are responsible for the coloration of the crystals but the nature of the color centers still remains poorly explained. Investigations of oxides with the K_2NiF_4 structure have revealed that deviations in oxygen nonstoichiometry cannot be attributed to the presence of intergrowth phases or deviations in the metal ratio [1]. In some papers the deformation of AlO_6 (GaO_6) octahedra in perovskite structure is also predicted. The nature of point defects depends mainly on the protective atmosphere during crystal growth, and their formation is associated with structure changes, and changes in the valency of ions and their electronic structure.

The purpose of the present paper is to report the relationship between dissociation products of compounds, protective atmosphere, reaction with crucible material and crystal properties. The results obtained by X-ray photoelectron spectroscopy (XPS) studies are reported to explain the role of the protective atmosphere on the electronic structure of ions. The spectra of cations (Sr, La and Al) are almost the same for all "as-grown" crystals of perovskite-type structure grown at various oxygen pressure. The electronic structure of Ga and oxygen (and Pr) depends on the composition of the protective atmosphere. An additional spectra of O *1s* is observed for oxidized crystals. The interstitial oxygen was reported for perovskite crystals like $La_2NiO_{4+\delta}$ [2]. In the crystals containing cations of various valency like Pr (3^+, 4^+) its electronic structure depends on oxidizing atmosphere. Single crystals of $ABCO_4$-type pseudoperovskite structure such as $SrLaGaO_4$ (SLG), $SrLaAlO_4$ (SLG) and $SrPrGaO_4$ (SPG), and perovskite-like $YAlO_3$ (YAP) and $LaGaO_3$ (LG) are considered. Results of the dissociation of the compounds and the properties of the crystals are compared with crystals of different structure containing gallium and aluminum ions.

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MICRO-CHANNEL EPITAXY OF GaAs BY MOLECULAR BEAM EPITAXY

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Microchannel Epitaxy(MCE) is a new technology the aims of which are firstly to grow dislocation free epitaxial layers on largely lattice-mismatched substrate and secondly to get a semiconductor -on-insulator(SOI) structure. MCE is consisted of selective area epitaxy(SAE) and epitaxial lateral overgrowth (ELO). The published works on ELO appeared rather early in the history of epitaxy [1-2]. However, the objective of the earlier works is to get SOI structure and not to reduce the dislocation density. We have shown in 1988 that this technique can be used to reduce the dislocation density[3].

The concept of this technology is expressed as follows. By covering all the substrate with amorphous film such as SiO_2 and Si_3N_4 and cutting narrow windows(we call this as microchannel) by lithography technique, one can prevent the propagation of dislocations from the substrate when epitaxial growth from the window and successive growth in lateral direction is conducted. Namely, lattice information is transferred through the microchannel from the substrate to epitaxial layer while defect information is prevented to transfer by the presence of amorphous film. On the other hand, in the case of normal epitaxy, both of lattice information and defect information is transferred to epitaxial layer. By decreasing the width of the microchannel down to the order of 10 nm one can decrease the dislocation density nearly to zero even microchannel is open and one can separate the epitaxial layer from the substrate electrically even epitaxial layer and substrate are connected through microchannels.

In the present talk MCE by MBE is presented. It is well known that SAE of GaAs is difficult by MBE because polycrystals are easily deposited on the SiO_2 mask. Recently, we found that by using low angle incidence of molecular beams, it is possible to conduct SEA much more easily compared with conventional MBE[4]. By using low angle incidence molecular beams we successfully achieved MCE by MBE. We call this technique as LIMCE(Low angle incidence beam microchannel epitaxy). LAIMCE was conducted with microchannels in radial arrangement and it was found that the with of lateral growth depends both on the crystallographic orientation of the microchannel and the direction of the Ga and As beams with respect to the microchannel orientation[5]. By optimizing the growth condition we obtained the MCE layer of 1.5 μm wide and 70 nm thick over SiO_2 mask[6].

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COMMON FEATURES OF GALLIUM PEROVSKITES SOLID SOLUTIONS

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Single crystals of gallium perovskites solid solutions with rare earth elements La, Pr, Nd and Sm. have been grown by the Czochralski and floating zone methods. The segregation coefficients of Pr, Nd and Sm in $LaGaO_3$ based single crystals have been determined in the crystals grown by the Czochralski method using Electro Probe Microanalysis.

The structure of the crystals has been investigated by powder X-ray, synchrotron radiation and neutron diffraction methods. The usage of various diffraction methods allowed us to determine position of atoms in the unit cell and evolution of perovskite lattice deformation induced by continuously varying average rare earth ionic radius. It has been found that the unit cell volume at room temperature varies from approximately 227 to 236 $Å^3$ in $SmGaO_3$ and $LaGaO_3$ respectively. Substituting of lanthanum by smaller ions thus the decrease of the unit cell volume causes rotation and deformation of GaO_6 octahedra.

The structure of the crystals have been also investigated at low and elevated temperatures in order to determine the anisotropic thermal expansion coefficients that might be of interest in case of application of these materials as substrates for epitaxy of high temperature superconductors.

Crystals containing lanthanum undergo first order structural phase transition from Pbnm to R3c symmetry at sufficiently low admixture of the other rare earth element. The temperature of the phase transition in the solid solutions has been determined by differential thermal analysis.

We have found that the unit cell parameters including atoms positions, thermal expansion coefficients, segregation coefficients and phase transition temperature scale with the unit cell volume in all investigated crystals. All these parameters may be represented as a function of average ionic radius of rare elements however this value is not well determined in these compounds because of ill determined coordination number.

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X-RAY HIGH-RESOLUTION DIFFRACTOMETRY FOR STUDIES OF SEMICONDUCTOR MATERIALS

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X-ray diffuse scattering is a powerful tool to study small, statistically distributed defects in otherwise perfect single crystals [1]. Full calculations of reciprocal-space intensity maps for defects of spherical symmetry and dislocation loops were presented in [2]. Recently successful comparisons of simulated maps and experimental results obtained with high-resolution diffractometry were published [3–6]. The present paper reviews the older and newest articles and demonstrates the perspectives of further studies for specific semiconductor materials. It seems that very important are investigations of correlations of spatial distributions of microdefects as well as correlation functions of the incident beam (partial-coherence phenomena). Other problems include the Fourier transforms of these correlation functions which should improve the agreement between the simulated and experimental results. These issues will be reviewed and discussed in the present paper.

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X-RAY CHARACTERISATION OF SELF-ORGANISED MESOSCOPIC STRUCTURES

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Mesoscopic semiconductor structures with dimensions in the nanometer range have an impressive potential for e.g. future optoelectronical applications. Zero-dimensional structures ('quantum dots') that are confined in three dimensions are presently the main subject of respective research. Self-organised epitaxial growth mechanisms are often applied to fabricate arrays of strained, coherent, and highly regular nanoscale islands. Despite of the huge efforts of many research groups their growth is, however, still not well understood.

X-ray diffuse scattering is an excellent tool (i) to investigate positional correlation within arrays of mesoscopic structures and, (ii) to characterise the strain field inside and around such structures with high sensitivity. It is complementary with direct imaging techniques in so far it statistically averages over large ensembles.

Grazing incidence small angle scattering (GISAXS) is highly sensitive to positional correlation, shape and size of mesoscopic structures while it is insensitive to strain, whereas high resolution x-ray diffraction (HRXRD) and grazing incidence diffraction (GID) are dominated by strain. The combined use of these different scattering techniques for the evaluation of positional correlation and strain will be presented for several mesoscopic systems.

In case of SiGe islands grown on Si(001) it will be demonstrated that HRXRD reveals details of the spatial Germanium distribution inside such islands. The implication of these findings for the island growth will be discussed together with respective atomic force micrographs that are recorded at identical and other similar structures.

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EFFECT OF IMPURITIES ON THE GROWTH KINETICS OF CRYSTALS

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Crystal growth is affected profoundly by impurities. Most of impurities suppress growth, while some few impurities enhance it. Some can stop growth completely even at very low impurity concentrations less than one ppm. Impurities usually act on certain crystallographic faces. The effect depends on impurity concentration, supersaturation and temperature. It also depends on the impurity present and the system concerned. Thus, the impurity effect on crystal growth varies widely [1-3]. This contribution discusses the effect of impurities on the kinetics of crystal growth, mainly in aqueous solutions, in the light of the model proposed by Kubota and Mullin [4]. In this model [4], impurities are assumed to be adsorbed on the step lines at kink sites following the Langmuir mechanisms for inhibition of step displacement with a modified pinning mechanism. Effects of impurity concentration [4, 5, 7, 8], temperature [4, 5, 7, 8] and supersaturation [6, 9] on impurity action for the crystal growth are discussed reasonably for different crystallizing systems with different impurities. The impurity action is characterized by the impurity effectiveness factor, which is defined as a function of edge free energy, dimension of growth unit, temperature, supersaturation and the spacing between neighboring active sites for impurity adsorption. An adsorption isotherm of lead (II) impurity determined from the analysis of growth data of potassium chloride crystals is well compared [8] with that obtained from direct adsorption experiments to verify the validity of the model. Unsteady state behavior of crystal growth rates in the presence of impurities is also discussed [9, 10].

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HOMOEPITAXY OF METAL GROUP III NITRIDES: APPLICATION TO OPTOELECTRONICS

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Gallium nitride and related ternary compounds AlGaN and InGaN attract a large attention because of applications in green/blue/ultraviolet optoelectronics, high temperature/high power electronics, as well as because of interesting physical properties of these materials, different to other semiconductors.

One of the most important problems in nitride technology is lack of easily available lattice-matched substrate for epitaxial growth. The commonly used substrates, sapphire and SiC, have large lattice mismatches (16% and 3.5%, respectively) and cause creation of a dense dislocation network.

Surprisingly, these dislocations do not lower the efficiency of green/blue light emitting diodes (LEDs), which are already commercially available. Small influence of dislocations in that case has its origin in special properties of indium atoms which have a tendency to be segregated (to form nanometric objects with higher In concentration) and to bind holes which take part in luminescent recombination in low excitation regime (as in LEDs).

For high excitation regime (as in lasers), dislocations play a detrimental role. Therefore, many labs conduct an extensive research to grow single crystals of gallium nitride which would be used as substrates in nitride technology. It is a very difficult task because of thermodynamical properties of this compound. At 1 bar of ammonia, it decomposes at about 1300 K, whereas its melting point is at least twice larger (at 45 kbar). In our Center, I. Grzegory and her group have developed a technology of an efficient growth of GaN crystals at about 1800 K and 10-20 kbar. These crystals have a record size (more than 100 mm^2) and the lowest dislocation density of 10-103 cm^{-2}.

In my talk, I will show advantages of using these bulk crystals as substrates for nitride epitaxy over sapphire or SiC. I will present the experimental results from the following techniques:

1. atomic force microscopy (AFM) indicating a non-disturbed step-flow growth mode,
2. X-ray diffraction (XRD) rocking curves proving an excellent crystallographic quality over a large area,
3. transmission electron microscopy (TEM) showing dislocation-free material,
4. photoluminescence (PL),
5. electroluminescence (EL).

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INTERFACE FORMATION BETWEEN ORGANIC SEMICONDUCTOR FILMS AND INORGANIC SEMICONDUCTOR SUBSTRATES

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Films of the organic molecule 3,4,9,10-Perylene TetraCarbocylic DiAnhydride (PTCDA) were deposited by Organic Molecular Beam Deposition (OMBD) onto the semiconductor substrates silicon (Si) and gallium arsenide (GaAs). The (100) oriented substrates were passivated by hydrogen and sulfur for Si and GaAs, respectively. Growth was performed using various substrate temperatures in the range from 230 to 470 K in an ultra-high vacuum chamber equipped with low energy electron diffraction/Auger spectroscopy facilities and optically aligned a multi-channel Raman spectrometer. The substrate temperature during growth was derived from the temperature induced Raman shift of the substrate phonon features. For each temperature the same PTCDA film thickness of approximately 40 nm was prepared. Thereafter Raman were recorded in the range from 25 to 2000 cm^{-1} using a photon energy of 2.54 eV (Ar^+ ion laser) which is suitable for resonance enhancement of the PTCDA Raman response. Above 200 cm^{-1} the Raman spectra show the features due to scattering by the internal vibrational modes of the PTCDA molecule. According to symmetry considerations the 19 A_g modes dominate the spectra under resonant excitation conditions. The formation of crystalline domains leads to the occurrence of two-fold Davydov splitting as two molecules from the base of the monoclinic unit cell. This effect is most markedly observed for a mode at 233 cm^{-1} which has dominant contributions of the C-O stretch vibrations. Its splitting is compared to that of a PTCDA single crystal. A further consequence of crystallinity is the appearance of external modes, or in other words libronic type phonons in the low frequency range below 200cm^{-1}. All six expected modes are observed and the changes in their frequency and full width at half maximum indicates improving crystallinity with increasing substrate temperature. Moreover, the crystallinity is further improved when GaAs is used as a substrate. However, the films deposited do not form single crystal layers but are polycrystalline as clearly confirmed by atomic force miroscopy measurements. The size of individual crystals dramatically increases with substrate temperature. This also explains the increase in photoluminescence yield and surface roughness with increasing substrate temperature both also being detectable in the Raman spectra.

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APPLICATION OF OPTICAL SPECTROSCOPY METHODS TO STUDY OF THE ORIENTATIONAL ORDER IN LIQUID CRYSTALS

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The fundamental feature of the liquid crystalline phases is the existence of a degree of long-range positional and/or orientational order intermediate between that of the completely ordered solid and the disordered isotropic liquid. The long-range order usually leads to anisotropies in the physical properties of liquid crystals, which may be used to determination of the degree of order. Moreover, liquid crystals as well orienting solvents are particularly suited for investigation of dissolved guest molecules. These both kinds of investigations can be carried out by using polarized light spectroscopy methods. Linearly polarized light is of special interest because it represents a powerful tool for study of oriented assemblies of molecules, such as crystals, thermotropic and lyotropic liquid crystals or lipid bilayers [1].

Here, the following spectroscopic methods using linearly polarized light will be briefly reviewed: infrared (IR), visible (VIS) and ultraviolet (UV) absorption spectroscopy, fluorescence depolarization (FD) and Raman scattering (RS). It will be shown, that using these methods one can obtain information about the long-range orientational order, intermolecular interactions and dynamics of molecular motion in liquid crystalline systems [2-4]. Particular point will be made about investigations of the guest-liquid crystal mixtures, because they can be utilized in two ways: to determine the molecular spectroscopic properties of the guest molecules, for example the polarization of the electronic absorption and emission transitions in UV, VIS and fluorescence spectroscopy or vibrational transitions in IR and RS spectroscopy [1,2,4] on the one hand and to characterize the structure of the uniaxial liquid crystalline phases on the other [2-4]. In this latter case the guest molecules can be used as probes to reflect the orientational properties and dynamics of the host medium.

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CRYSTAL GROWTH OF FLUORIDES

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A new, highly reproducible crystal growth technique for high quality fluorides has been developed. A series of fluorides free from cracks and inclusions has been grown for UV and IR optical applications. Crystal growth was performed in a Czochralski furnace with atmospheric control system. High vacuum (approximately 10^{-5} torr) prior to the growth and CF_4 gas atmosphere during growth were applied. By employing these conditions, undoped and Ce-, Tm- and Ho-doped $LiCaAlF_6$, $LiSrAlF_6$, $LiSrGaF_6$, $LiYF_4$, $LiLuF_4$, $KMgF_3$ and $BaLiF_3$ single crystals 25mm in diameter and 80mm in length were successfully grown, without any HF purification and fluorinating process. Subsequently, larger single crystals 50 mm (2-inches) and 75 mm (3-inches) in diameter have also been successfully grown, without any inclusions and cracks. 60 mJ and 27 mJ pulses in the UV wavelength region were generated using Ce:$LiCaAlF_6$ and Ce: $LiLuF_4$ single crystals. To the authors' knowledge, these performances are the highest ever reported for all-solid-state UV lasers. Since the $LiCaAlF_6$ crystal showed high transmission down to 112 nm, it represents an ideal optical window material for next-generation optical lithography technology with shorter wavelengths such as 157 nm (F_2 laser) and 126 nm (Ar_2 laser). $KMgF_3$ and $BaLiF_3$ single crystal were also found to be a promising new material for this application. The advantages of these crystals are: (1) no birefringence (2) possibility of growing large crystals (3) shorter transmission edge. Tm,Ho:$LiLuF_4$ and Tm,Ho:$LiYF_4$ Single crystals were diode pumped at 792 nm, at room temperature, to generate 2μm eye-safe laser. Pulsed Output energies, at 1 Hz, up to 13.5 mJ and 9.9 mJ were obtained for 255 mJ of incident pump energy, respectively.

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STRUCTURE AND MAGNETIC PROPERTIES OF METALLIC MULTILAYERS EXHIBITING GIANT MAGNETORESISTANCE EFFECT

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The last decade witnessed an increase in the interest in metallic multilayer structures composed of alternately deposited ferromagnetic (F) and non-ferromagnetic (NF) thin metallic films. This interest is a direct consequence of a discovery of two phenomena in such structures: oscillatory exchange coupling leading to parallel or antiparallel configuration of magnetisation in neighbouring F sublayers as a function of NF sublayer thickness and considerable changes in electric resistance as a function of external magnetic field R(H), known as the giant magnetoresistance (GMR) effect. These phenomena were initially observed in multilayered films obtained by the molecular beam epitaxy method, but soon they were also found in samples obtained by evaporation or cathode sputtering.

The paper presents results of structural (X-ray diffraction and atomic forces microscopy) and magnetic (hysteresis loop measured by vibration magnetometer, magnetooptical Kerr effect and magnetoresistance) studies of multilayer F/NF systems with F=$Ni_{80}Fe_{20}$, Co; NF=Cu, Ag, Au, obtained by sputtering. The influence of the kind of F and NF, thickness of the sublayers, type of substrate and buffer layer on the structure of the systems has been investigated. The correct choice of these parameters has been proved to lead to different R(H) dependencies, suitable for particular applications. The influence of imperfections in the multilayer structures such as roughness of the interfaces and discontinuities of NF type sublayers, on the coupling and size of GMR is discussed.

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GROWTH AND DOPING OF SINGLE CRYSTALS OF GaN AND AlN UNDER HIGH NITROGEN PRESSURE

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Single crystals of gallium nitride (GaN) and aluminum nitride (AlN) are getting considerable attention lately because of its application as substrates for very bright light emitting diodes and lasers in the blue segment of the color spectrum. One of the most promising and useful methods to obtain high quality GaN substrates is High Nitrogen Pressure Solution Growth (HNPSG). This method can also be used for AlN crystallization.

This work presents the resent results of gallium nitride and aluminum nitride crystal growth just by the HNPSG method. It is well known that for GaN the nitrogen pressure allows to extend the stability range up to the temperature, where effective crystallization from the solution is possible. Therefore, GaN crystals are grown at pressures of 1÷2 GPa and temperatures of 1800-2000 K. The growth without an intentional seeding results in hexagonal platelets of average size higher than 1 cm^2. The seeded growth also gives the promising results. In this work GaN seeded growth into {11-20} and {0001} polar directions is reported.

The GaN crystals obtained from base gallium-nitrogen solution are strongly n-type due to unintentional oxygen doping. Addition of magnesium or beryllium into the growth solution eliminates the free carriers in gallium nitride. In effect, the p-type or highly resistive material can be synthesized. The basic properties of GaN:Be and GaN:Mg crystals are discussed in this paper.

From the thermodynamic point of view, high N_2 pressure is not necessary for AlN crystal growth. At nitrogen atmospheric pressure AlN is stable up to 2800 K. However, at N_2 pressure up to 650 MPa, the combustion synthesis of aluminum nitride has been observed. In order to avoid the combustion reaction, the increase of N_2 pressure becomes important. Due to the high thermal conductivity and high heat capacity of gas at high pressure, the complete extinction of the combustion process is possible and the crystal growth of AlN from the solution can take place. The needle-like and plate-like AlN crystals up to few millimeters have been obtained at pressure of 1 GPa and temperatures up to 2000 K. The AlN growth without an intentional seeding is compared with the similar GaN crystal growth process. The influence of temperature, pressure and supersaturation on habit and morphology of both nitride crystals is also discussed and compared.

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NANOSTRUCTURES TECHNOLOGY BY MOVPE TECHNIQUE

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The Metal Organic Vapour Phase Epitaxy (MOVPE) is one of the most advanced epitaxial growth techniques used in semiconductor research an development laboratories. This method has allowed access to new device phenomena by producing different kind of heterostructures with extremely fine dimensional, compositional and doping control. This precise control is especially important in optoelectronic and microwave devices technology. A large number of new device concepts are based on low dimensional structures (nanostructures). Thus, a major goal for advanced devices technology is to gain a full control over the growth of a wide range different semiconductor nanolayers with excellent homogeneity and purity.

In the paper some advanced devices like Schottky diodes for 100 GHz range, MSM and PIN photodetectors for high frequencies application, with enhanced selectivity and sensitivity provided by a resonant cavity effect are presented and the related requirements for MOVPE technology are defined. Material thickness, doping and composition in such structures have to be controlled to a few (practically to one) atomic layers. Correlation between a MOVPE process parameters of AlGaAs/GaAs, InGaAs/GaAs, AlGaAs/sapphire low dimensional heterostructures and basic chemical phenomena are presented and discussed. The empirical formula which allowed to control the composition and growth rate (thickness) of undoped AlGaAs alloys is defined. Critical thickness and photoreflectance method for characterization of the strained InGaAs/GaAs structures are discussed.

Technological aspects of delta doping of GaAs, AlAs, and AlGaAs are presented. Optimal growth conditions for such layers growth and doping are described. Some problems of designing and fabrication of RCE photodetectors nanostructures are presented. Different kind of AlAs/GaAs Bragg reflector structures are shown and their characteristics are discussed.

Nowadays, a MOVPE technique is also used to work out the AlGaN/GaN heterostructures for high temperature electronic device application. The results of MOVPE growth of AlGaN/GaN heterostructures with 2DEG effect are presented and the alloy composition influence on sheet carrier concentration and mobility are discussed.

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THERMOANALYSIS OF LIQUID CRYSTALS

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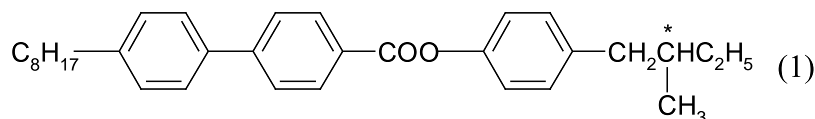
The studies of polymorphism of thermotropic liquid crystals by means of two thermoanalytic methods, polarisation thermomicroscopy and differential scanning calorymetry (DSC) are presented.

The classic classification of rod-like liquid- crystalline phases is given [1]. The examples of characteristic textures corresponding with the different structures of liquid crystals, obtained for chosen mesogenic compounds, are presented. Compounds with rich polymorphism, having at least six different liquid crystal phases (1) were studied by thermomicroscopic method. The sequence of registered textures was in conformity with their thermodynamic stability [2].



(1)

Cr 49.8 S_G 63 S_J 65 S_F 67 S_I 72 S_C 85 S_A 137 N^* 139 Blue 141 I

The method of co-miscibility was adopted for confirmation of phase identification. This method consists in a preparation of isobaric phase diagrams for two-compound mixtures containing a standard and studied compound [3].

Temperatures and enthalpies of phase transitions of mesogenic compounds of rich polymorphism were measured by DSC method. Measuring specific heat under constant pressure (by DSC) one could show a difference between phase transitions of the first and the second order (according to Ehrenfest) from one liquid crystal phase to another.

Moreover, the results of studies of compounds belonging to the antiferroelectric liquid crystals group [4] are presented.

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INVESTIGATION OF OPTICAL AND STRUCTUAL HOMOGENITY OF $Ca_4GdO(BO_3)_3$ SINGLE CRYSTALS

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Gadolinium calcium oxoborate $Ca_4GdO(BO_3)_3$ (GCOB) undoped single crystals can be used mainly in piezoelectronics. The GCOB crystals doped with rere- earth ions, e.g. with Nd and/or Y (also Eu, Er, Tm) are the new and promising laser materials [1].

In this work we investigate the optical and structural homogenity of undoped GCOB crystals grown from the melt by the Czochralski method in [010] direction. This homogenity is of the primary importance especially in all the optical applications of these crystals. The optical homogenity has been measured using an automated spectropolarimeter over the entire area of the samples in the wavelenght range of 660 – 800 nm [2] and reveled a fair to good optical quality of the investigated crystals. Those results have been compared with the surface etching experiments.

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THE INFLUENCE OF LATTICE MISMATCH AND GROWTH RATE ON THE DECAY OF RHEED OSCILLATION N THE CASE OF InGaAs/GaAs GROWTH

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In this work, we analyze the oscillations of the intensity of the RHEED (reflection high-energy electron diffraction) pattern as a function of InAs mole fraction during the initial stages of growth during molecular beam epitaxy of $In_xGa_{1-x}As$ on GaAs (001) surface. We focus on the growth front roughening during (quasi-) 2D pseudomorphic growth, that is, the regime *before* the 2D-3D transition and plastic relaxation. This regime of growth has received only limited attention, since most studies were focused on the onset of 2D-3D transition or lattice parameter change due to strain relaxation.

The oscillations' amplitude was found to decrease exponentially *versus* time during the InGaAs growth. Further, the decay time constant decreases with InAs mole fraction, indicating that the lattice strain increases islanding during growth. A simple semi-quantitative model based on the growth front roughening is formulated to explain the results. The model includes the effects of varing growth rate as well. Model parameters are determined for different growt parameters, and their physical reasoning is given. Limitations of the modelare discussed. Assuming that theoscillation decay is related partly to the strain and partly due to starin-independent kinetic effects during growth, a decay component that is solely due to strain can be separated. We find that onset of increased roughening due to misfit strain component roughly corresponds to the equilibrium critical layer thickness.

Acknowledgements

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THE CRYSTAL STRUCTURE OF THE URANIUM DIGERMANIDE UGe_2

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The phase diagram of intermetallic binary U-Ge compounds was investigated for last 40 years. They form an interesting series of compounds with properties ranging from ferromagnetism to superconductivity. However, a more through investigation of the available literature reveals many uncertainties about the crystal structures of these compounds. In the case of the uranium digermanide UGe_2 four types of crystallographic structures were considered: $ZrSi_2$ (Cmcm) [1], two types of $ThGe_2$ (Cmmm) [2, 3] and $ZrGa_2$ (Cmmm) [4]. Recent X-ray and neutron diffraction [3, 4] studies confirmed crystallization of the UGe_2 system in an orthorhombic type structure with Cmmm space group but details of atomic positions were different. Crystallization in $ZrSi_2$-type structure was finally excluded.

To determine the real crystallographic structure of the UGe_2 system an additional way, which is not depended on quality of sample, is proposed. Based on experimental crystallographic data (atomic positions and lattice constants) ab-initio electronic structure calculations were performed. These calculations allow reproducing of band structure of real systems for para- and ferromagnetic phase. Direct comparison of total energies showed that the most stable structure (having the lowest energy) is the $ZrGa_2$ one determined by Boulet et al. [4]. The statement is true for calculations performed for para- and ferromagnetic state and for different types of exchange-correlation potentials.

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LSAT - PROMISING SUBSTRATE FOR GaN EPITAXIAL GROWTH

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Mixed perovskite (La,Sr)(Al,Ta)O_3 (LSAT) is one of the most promising materials to prepare substrates for GaN epitaxial layers. In this work single crystals of LSAT were grown by the Czochralski method with use of the iridium crucible and passive afterheater. The obtained single crystals <111> orientation up to 20 mm in diameter and 50 mm in length were free of inclusions and macroscopic defects. The optical transmission was measured in the region 200 – 3000 nm . The measured unit cell parameter (a = 7,730 Å) well suit to GaN lattice in the case of <111> oriented LSAT single crystals. The chemical composition was checked by EPMA method . It was found that it is close to the stoichiometric one. With Lang transmission topography growth striations and dislocations were examined. Electrical conductivity and capacitance in dependence on temperature, hardness , thermal expansion coefficient and etch pits density were also measured.

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THERMODYNAMIC ANALYSIS OF THE GROWTH OF ALN AND GaN FROM VAPOR: NITROGEN AND METAL RICH CONDITIONS

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Electronic theory of the cohesion of binary III-V semiconductors will be used to define the contribution of the metal and non-metal component of enthalpy of vaporization of the crystals. Also the entropy contribution will be divided into the metal and non-metal parts.

The division will be used for the definition of the metal and non-metal-rich growth conditions in terms of the partial pressures of the constituents. The partial pressures corresponding to the low supersaturation growth condition will be calculated for group III metal nitrides: AlN and GaN. It will be shown that for AlN the metal rich conditions extends to the temperature T=3400K, i.e. close to the melting point. For GaN the metal rich condition can be achieved only for the temperatures below 1450K.

The decomposition of molecular nitrogen is catalyzed by metal surfaces. Therefore the condition formulated in this work, indicates that the growth of GaN from the vapor mixture of the constituents is difficult. This also indicates that AlN can be grown from the vapor much easier. These results are in agreement with the successful growth of AlN from the vapor and the disappointing results of GaN vapor growth attempts.

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PROBING THE NANOMECHANICAL PROPERTIES OF CRYSTALS BY ATOMIC FORCE SPECTROSCOPY

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We have studied the nanomechanical properties of brittle materials by combining indentation assays and topographic imaging of the surface with an atomic force microscope (AFM). As is shown in figure 1, force curves display discrete events that are related to the appearance of nanometer-sized indentations [1]. These "jumps" are associated with the number of atomic layers being expelled by the tip penetrating the surface. The actual effect on the sample (e.g. size and shape of the nano-indentation) can be subsequently obtained by imaging the same region (figure 1, inset). Such indentations do not produce any dislocation on the surface. The layered expulsion of material demonstrates that the critical stress of plastic deformation initiation corresponds to brittle failure. In addition, recent studies show that the recovery of the surface with time is mediated by humidity [2].

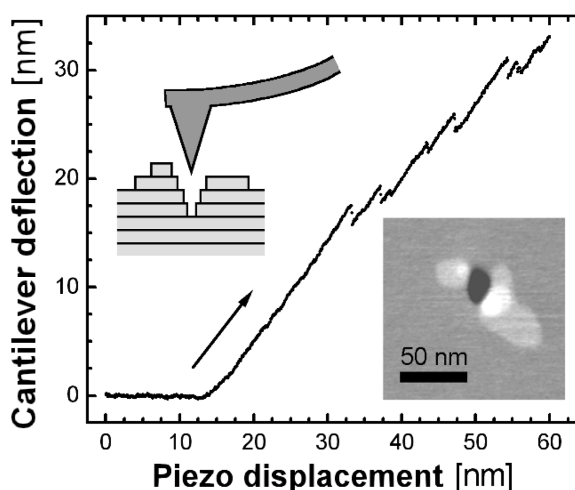

Figure 1: *AFM force curve recorded during an indentation assay on the surface of a MgO sample. When the curve displays discrete events ("jumps"), imaging the region reveals that a cavity surrounded by the expelled material has been produced.*

The novel results that will be presented include the detailed study of the elastic regime and the mechanics of the nanometer-sized contact region between the tip and the surface. The experimental data cannot be fitted by a hertzian behavior, and the difference becomes more obvious in harder materials (see black curve in figure 2).

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A new and simple model will be presented for the elastic contact, which provides a good fit of the experimental data (see figure 2, gray curve). It is based on a constant interaction area (diameter *d*) behaving as an equivalent spring in the surface plane (spring constant *K*). The projection of the force in the normal direction produces a progressive, nonlinear response. The parameters *K* and *d* are obtained from the fit, and allow to estimate both the elastic modulus and the mean effective Debye energy.

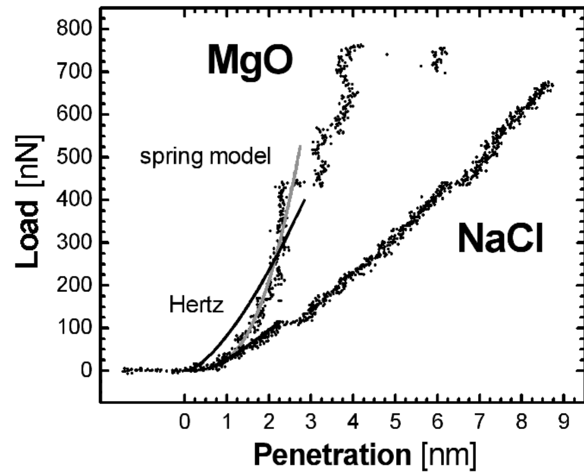

Figure 1: *Indentation curves showing the different mechanical properties of MgO and NaCl (elastic modulus, yield strength). Solid lines show the fit of the MgO elastic region to the classical hertzian (black) and to the spring model proposed (gray).*

The physical interpretation of the model and its application to other materials will be discussed. These findings are the result of combining local force spectroscopy measurements with the characterization of surface defects by AFM. Besides providing an accurate measurement of the mechanical properties of crystals and thin films, they may have important consequences on the theory of elastic contact between nanometer-sized regions.

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NEGATIVE MAGNETORESISTANCE FROM ELECTRON-ELECTRON INTERACTION EFFECTS IN InGaAs/InP HETEROSTRUCTURES

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Negative magnetoresistance has been widely observed at low temperatures in strongly doped semiconductors and other disordered electron systems with metallic conductivity. It is now clearly established that quantum corrections such as weak localization and electron-electron interaction are responsible for the appearance of this effect.

We have measured the magnetoresistance of two-dimensional electron gas in $In_{0.53}Ga_{0.47}As$/InP modulation-doped heterostructures in the temperature range 40 mK - 4.2 K. The electron density and mobility were $(0.4\text{-}4)\times10^{11}$ cm^{-2} and $(1\text{-}5)\times10^{4}$ cm^{2}/Vs respectively, the corresponding value of the product of the electron mean free path and of the Fermi wave vector $k_F l_e$, characterizing the strength of the disorder was in the range from 2 to 15. In magnetic fields less than about 1 T and before the onset of Shubnikov-de Haas oscillations a large negative magnetoresistance was recorded, which followed a quadratic dependence on the magnetic field. The magnitude of this parabolic negative magnetoresistance as well as its dependence on the temperature can be satisfactorily interpreted in terms of electron-electron interaction in two-dimension.

Acknowledgements

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GROWTH PROPERTIES OF Ti/Co MULTILAYERS

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Ti/Co multilayers (MLs) with uniform and wedge-shaped Ti or Co sublayers were prepared onto SiO_2/Si(111) substrates using UHV (5×10^{-10} mbar) DC/RF magnetron sputtering. The chemical composition and the cleanness of all layers was checked *in-situ*, immediately after deposition, transferring the samples to an UHV (4×10^{-11} mbar) analysis chamber equipped with Auger and X-ray photoelectron spectroscopy (AES, XPS). Growth of the Co sublayers on Ti was studied by standard UHV scanning tunnelling microscopy (STM) and spectroscopy (STS) at room temperature (RT). The structure of the MLs with uniform sublayers was examined *ex-situ* by standard θ-2θ X-ray diffraction. The magnetic characterisation of the samples was carried out using the magnetooptical Kerr effect at RT.

Results on systematic studies of high-angle X-ray diffraction as a function of Co and Ti sublayer thicknesses for Co/Ti MLs with d_{Co} and d_{Ti} greater than ~ 3 nm show that only (002) reflections of hcp Co and Ti are present in the patterns. The average Co and Ti crystallite sizes in direction perpendicular to the substrates, as determined from the Scherrer equation, are comparable to their respective sublayer thicknesses. Only a broad peak related to the Ti sublayers was observed for the MLs with $d_{Co} < \sim3$ nm and $\sim3 \text{ nm} > d_{Ti} > \sim2$ nm. For $d_{Co} < \sim3$ nm and $d_{Ti} < \sim2$ nm, practically no reflections were observed in the high-angle X-ray diffraction patterns. The absence of the Co reflections for $d_{Co} < \sim3$ nm is consistent with UHV STM images, which showed randomly oriented Co grains with an average size D ~ 3 nm. A significant drop of the coercivity with decrease in Co layer thickness - typically from H_c ~ 1-1.4 kA/m to H_c ~ 0.1-0.2 kA/m - was observed at a critical Co thickness d_{crit} ~ 3.0 (d_{Ti} = 2 nm) and 3.1 nm (d_{Ti} = 3 nm). The coercivity behaviour could be associated with the structural properties of the Co layer grown onto Ti. Cobalt sublayers grow in the soft magnetic nanocrystalline phase (D ~ 3 nm) for a thickness lower than the critical one. In that case, the average Co grain size is significantly smaller than the magnetic exchange length for the cobalt layer (L_{ex} ~ 10nm). For a thickness greater than the d_{crit}, the Co sublayers undergo a structural transition to the polycrystalline phase with average grains size D > 10 nm. Furthermore, we have estimated an average Co roughness from STM measurements as ±0.2nm and ±0.3nm for nanocrystalline and polycrystalline layer, respectively. The STM observation with atomic resolution revealed a high grains deformation of the nanocrystalline Co layer, in agreement with recent NMR studies.

Acknolwdgements

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APPLICATION OF X-RAY DIFFRACTION AND TOPOGRAPHY TECHNIQUES FOR STUDIES OF STRAIN IN LATERALLY OVERGROWN EPITAXIAL STRUCTURES

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Epitaxial lateral overgrowth (ELO) has been shown to reduce significantly dislocation density in epitaxial layers grown on lattice mismatched substrates. The breakthrough in development of long life GaN/InGaN blue lasers, being due to the high efficiency of defects filtration during lateral growth, is the most spectacular recent achievement of the ELO technique. Although ELO layers are structurally of much higher quality than the planar buffers deposited directly on the substrate they are not free of strain. In particular, mask covering the substrate, lattice and thermal expansion mismatches of subsequent layers and the substrate may lead to large deformations of ELO layers. Indeed, it is commonly observed that the lattice planes in laterally overgrown parts (wings) of the layers exhibit crystallographic tilt from that in the seeding region. This creates significant problems for coalescence of neighbouring stripes. Therefore, there is much effort to reduce wing tilt and to improve quality of the coalescence front by optimisation of growth parameters. To reach this goal, however, methods of measuring of ELO lattice planes tilt are required. The aim of this work is to show that high resolution X-ray diffraction can be efficiently used to determine direction of tilt of ELO wings and to measure value of the tilt angle if specific geometry of ELO samples is taken into account. Then, evidence is presented that synchrotron X-ray topography technique with appropriate computer simulations can be a powerful tool for precise analysis of distribution of ELO lattice planes curvature across the ELO stripe. Experimental data on X-ray diffraction and X-ray topography studies of GaAs ELO layers grown by liquid phase epitaxial lateral overgrowth on GaAs and GaAs-coated Si substrates will be used as example.

Acknolwdgements

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THE ROLE OF F – ELEMENTS IN InP-BASED MATERIALS

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Rare earth (RE) elements have attracted attention in the context of semiconductor technology since about mid-1980s. The early expectations of efficient electroluminescent light sources due to RE centers incorporated in the heterostructure active layer has not been fulfilled yet. Nevertheless, their optical properties have been widely investigated, because RE doped semiconductors can potentially be used to fabricate optical devices that are insensitive to the surrounding host environment and because the excitation and de-excitation mechanism of RE^{3+} ions in the semiconductor host is an interesting physical phenomenon. Another strong motivation to study RE in the context of III-V compounds is their high chemical reactivity and reduction capability. It suggests a possibility to use these elements as efficient agents in removing undesirable residual impurities. The development of InP solid state particle detectors, realisation of InP microwave devices destined for very high frequency operation and fabrication of optoelectonic components are several examples for new interest in the preparation and study of InP and InP-based semiconductor layers and structures.

We report the effect of Pr, Nd, Ho, Er, Tb and Yb additions during the epitaxial growth on the resulting structural, electrical and optical properties of InP layers. Epitaxial layers were grown by Liquid Phase Epitaxy (LPE) on (100)-oriented InP:Fe and InP:Sn substrates from the melts containing besides essential components, also 0 - 0.4 wt% of RE element admixture. The growth process was commenced under flowing high-purity hydrogen at 640-660 °C with a cooling rate of 0.7-0.8 °C min^{-2}. To reduce the great affinity of RE especially with respect to oxygen and hydrogen, it was necessary to prevent the reactive metallic RE from the surrounding ambient at the stage before the growth process by mechanical embedding in the melt.

The grown layers were examined by scanning electron microscopy, Rutherford backscattering spectrometry, temperature-dependent Hall effect and low-temperature photoluminescence spectroscopy. The behaviour and the impact of individual f-elements were compared. We have demonstrated that the shallow donors are reduced effectively by up to three orders of magnitude. Room temperature Hall effect measurements revealed *p*-type conductivity of the layers prepared from the melt containing Pr or Tb admixture. The hole concentration was $6x10^{14}$ cm^{-3} and mobility 150 $cm^{-2}V^{-1}s^{-1}$. Photoluminescence spectra have been markedly narrowed, and fine spectral features have been resolved. Intracenter 4f-4f sharp luminescence transitions of Yb^{3+} have been observed in the case of Yb addition, thus confirming the incorporation of Yb^{3+} ions into the host lattice.

Acknolwdgements

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KINETICALLY DETERMINED PHASE TRANSITIONS IN SIDE CHAIN LC POLYMERS

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The transition between liquid crystalline (LC) phases in polymers are usually considered as being thermodynamically controlled, in contrast to the kinetically controlled crystallization from an LC phase; and the kinetics of the mesophase formation is mostly disregarded. We have found however at least three examples of kinetically driven phase transitions in side chain LC (co)polymers.

Our systematic study shows that the Sm B – Sm H transition in a copolysiloxane, the Sm A – Sm C* transition of a chiral polysiloxane, and the formation of a short pitch TGB A* phase in a series of chiral copolymethacrylates obey the same generic rule: both the transition temperature, T_m, and transition enthalpy, ΔH_m, grow with the time of isothermal annealing at temperatures, T_a, within the range 15 - 45°C achieveing saturation after 10-24 h of the annealing. The Avrami analysis of corresponding kinetic curves suggests diffusion-controlled phase formation (the Avrami exponent value, $k \sim 0.3 – 0.4$) or free two-dimensional phase growth ($k \sim 2$).

For the samples annealed until the corresponding phase transition is completed, the limit values of transition temperatures, T_m^∞, are linear upon the annealing temperature similar to crystallization of amorphous polymers. In contrast, the limit values of transition enthalpy, ΔH_m^∞, generally achieve maximum values at lower annealing temperatures but fall down, as the T_a increased. The suggested explanation is based on higher concentration of phase growth nuclei at lower temperatures that results in larger proportion of the substance involved into the phase transition, i.e. higher ΔH_m^∞ values, but at the same time, in smaller dimensions of the phase domains, i.e. in lower T_m^∞ values.

Acknowledgements

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STRUCTURE OF OXYGEN - IMPLANTED SILICON SINGLECRYSTALS TREATED AT ≥ 1400K UNDER HIGH ARGON PRESSURE

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Separation by Implantation of Oxygen (SlMOX) is now a well developed technology to produce silicon - on-insulator material. However, some aspects of that technology deserve further investigation, between them the recently [1] stated effect of external stress (exerted by enhanced hydrostatic pressure of gas ambient at annealing) on creation of SiO_2 and crystallographic defects in silicon implanted with oxygen, Si:O.

Structure of oxygen - implanted (up to a dose $6x10^{17}$ cm^{-2}) single crystalline silicon, treated at 1400 - 1550 K (HT) under argon pressure (HP) up to 1.2 GPa (HT - HP treatment), was investigated by Transmission Electron Spectroscopy (TEM), Secondary Ion Mass Spectrometry (SIMS), Infrared (FTIR), photoluminescence (PL) and X - ray methods.

Among the effects observed in Si:O after the HT - HP treatment are the following:

- the concentration of extended defects (dislocations) is markedly lower (TEM results);
- the oxygen distribution peak is of markedly lower height (SIMS results);
- the intensity of D 1 and D2 dislocation - related PL lines decreases with HP;
- the peak intensities and positions in Si-O-Si asymmetric stretching vibrational mode are changing with HT and HP (FTIR results);
- the defects created at HT - HP are of lower dimensions (in comparison to that in the Si:O samples annealed at 10^5 Pa, X - ray results).

The observed effects can be related in part to stress - dependent enhancement of oxygen diffusivity at HT - HP and to HP effect on the misfit at the defect / matrix boundary.

Acknowledgements

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STUDIES OF PIEZORESISTANCE AND PIEZOMAGNETORESISTANCE IN Si WHISKERS AT CRYOGENIC TEMPERATURES

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Silicon whiskers having 20-40 μm in diameter were studied in the wide temperature range down to 1.7 K. The crystals were obtained by the method of chemical transport reactions and doped by boron during their growth to concentrations 8×10^{17} - 1×10^{19} cm^{-3}. The temperature dependence of the crystals' resistance have been measured as well as their piezoresistance and piezomagnetoresistance at 4.2 K.

To provide both compressive and tensile strain of the whiskers they were mounted on spring elements. The conditions of the surface (bi-axial) thermal strains and stresses have been analysed in terms of the Hookian relation and stiffness constants transformed to the local <111> coordinate system of the crystal.

Starting from the thermal strain in a mounted whisker, the temperature dependence of the whiskers' resistance before and after the mounting on the substrates were compared. It has been shown that the thermal strain at liquid helium temperatures could be high enough to 'throw' a crystal from the metallic side of the metal-insulator transition (MIT) to insulating one and vice versa.

The negative magnetoresistance (NMR) in p-type silicon whiskers has been found at 4.2 K. The transition of the NMR to 'anomalous' positive magnetoresistance (PMR) at uniaxial compression applied was observed. A brief discussion of this phenomenon is presented.

The 'giant' piezoresistance (the longitudinal gauge factor $G_{<111>}=\Delta R/(R_o\times\varepsilon)$ up to 10,000-20,000) which was found in the vicinity to the MIT was applied in the strain gauges and pressure sensors having a very high sensitivity to the measured value.

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PREPARATION AND PROPERTIES OF (Fe,Zn) AND (Ti,Zn) CO-DOPED AND Mn DOPED INDIUM PHOSPHIDE SINGLE CRYSTALS

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Semi-insulating (SI) indium phosphide is important material for nuclear particle detectors, high-frequency devices, optoelectronic integrated circuits and other applications. Conventional SI InP is usually prepared by the iron doping in the concentration range 2 to $9\times10^{16}cm^{-3}$. However, large Fe concentration leads to deterioration of the crystall quality. To reduce the iron doping a careful pre-compensation with shallow acceptor can be used. If the N-type background concentration of undoped single crystals was about $9\times10^{15}cm^{-3}$ then zinc concentration was chosen about $8\times10^{15}cm^{-3}$ and the iron concentration was then 1 to $2\times10^{16}cm^{-3}$. To reach the resistivity of 10^5ohm.cm the titanium doping can be used, but there is a problem with the formation of the scum on the melt level surface. Manganese creates the energy level 0.24 eV above the valence band and thus it is possible to obtain P-type InP with higher resistivity. InP single crystals were grown by the computer controlled Czochralski (LEC) method. The polycrystalline material was synthesized by modified low pressure vertical Brigdman method. Single crystals were grown in the B/111/ orientation at the growth rate 15 mm/h. The crystal rotation was 10 rpm and crucible rotation 5 rpm. Boron oxide was vacuum treated at 1000°C for 6 hours just before pulling and creates 18 mm thick layer on the InP melt. InP:Ti crystals were grown from specially modified quartz crucibles to ensure the position of the titanium wire at the bottom of the crucible. The van der Pauw and DLTS measurements were used for the characterization of the material. Typical electrical parameters are in the table.

InP Crystal	Dopant Atom	Resistivity (Ωcm)	Mobility ($cm^2V^{-1}s^{-1}$)	Concentration (cm^{-3})	Conduct Type
G199	Fe/Zn	5.8×10^7	1713	6.2×10^7	N/P
G203	Fe/Zn	4.1×10^7	2805	5.4×10^7	N/P
G205	Fe	2.7×10^7	3113	7.5×10^7	N
T57	Ti/Zn	1.7×10^5	1625	2.3×10^{10}	N
G256Z	Ti/Zn	3.6×10^5	2371	7.4×10^9	N
G222	Mn	3.2	120	1.6×10^{16}	P
G223	Mn	4.8	91	1.4×10^{16}	P

The Hall coefficient of co-doped (Fe,Zn) InP reaches an extremum at 250 K and changes sign at about 235 K.

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VAPOUR PHASE PREPARATION AND DEEP LEVELS INVESTIGATION OF SEMIINSULATING CdTe:Cl SINGLE CRYSTALS

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Over the past decade CdTe were developed as a material for fabrication X-ray and γ-ray detectors operating at room temperature. These needs structurally perfect monocrystals with resistivities $\rho \geq 10^8\ \Omega\cdot$cm

The abstract reports vapour phase method to obtain semiinsulating CdTe:Cl single crystals Growth process was performed in two steps chemically homogeneous charge synthesis and first-hand single crystal formation. Single crystals were grown in evacuated quartz ampules of special form placed in vertical furnace with temperature profile ensuring growth rate equal to the velocity of ampule moving up (~0.2 mm/h).

Rather large (18mm in diameter, 40mm length) structurally perfect single crystals were obtained by this technology. Resistivities of the crystals with Cl concentration in initial source of $(10^{18} \div 10^{19})$cm^{-3} range have had values $\rho = (3 \div 4)\cdot 10^8 \Omega\cdot$cm at room temperature. Hall measurements at 300K showed the following parameters: major carrier (electrons) concentration $n=(5 \div 7)\ \cdot 10^7$ cm^{-3}, their mobility $\mu_e=300 \div 400$cm^2/Vsec. Prepared crystals were detector-grade.

To determine the deep levels location playing an important role on the electrical as well as transport characteristics some electric and fotoelectric measurements were carried out. It was found that obtained crystals conductivity was controlled by levels E_c-0.66eV, which often connected with native defect - Cd vacancy. Their concentration was evaluated to be $\sim 2\cdot 10^{15}$cm^{-3}.

Photoluminescence spectra of fabricated crystals consisted of dominant exitonic line and wide band 1.4eV, which corresponds to the donor-acceptor (Cl levels - A-centres) transition.

Intensivities of these bands were almost not changed for different parts of the same crystals, which demonstrate good homogeneity of prepared single crystals.

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NEW SEMICONDUCTOR COMPOUND ZnCdHgTe: GROWTH AND PROPERTIES

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The abstract reports newest data on physical and electrical properties of new semiconductor compound ZnCdHgTe (quaternary solid solution grown by modified LPE technique on (111) CdTe single crystal substrates). Epitaxial heterostructures $Zn_xCd_yHg_{1-x-y}Te$/CdTe were fabricated from Te-rich solutions and stoichiometric melts. Results of experiments presented in the paper allowed to ascertain the dependence of $Zn_xCd_yHg_{1-x-y}Te$ solid solutions band gap on composition (*x, y*). The main growth peculiarities as well as electrical characteristics measured at room temperature in range of applied voltage $V_a=0\div3$ V are described. Principal attention was focused on current-voltage (I-V) and capacitance-voltage (C-V) examinations because of their importance for further using in microelectronics applications. I-V studies revealed the intricate mechanism of carriers transfer through the interface epilayer/substrate: superposition of S-like and exponential portions of current-voltage dependencies was observed in forward direction of applied voltage and *velocity saturation mode → mobility regime* processes were realized under reverse bias. C-V examinations demonstrated an appearance of extended transition region of various composition localized in the epitaxial layer as well as in the wide-gap substrate. Both linear and step-like carriers distributions in the base of investigated structures were also found. Results of numerical experiment (in particular, numerical simulation of I-V and C-V dependencies) performed according to the obtained data are presented.

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FAR INFRARED SPECTRA IN TETRAHEDRAL QUATERNARY ALLOYS

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Far infrared (FIR) multi-mode phonon spectra enable us to determine real crystalline structure of semiconductor solid solutions. Kozyrev et al. [1] attribute lattice spectra of $Cd_{1-x}Hg_xTe$ (MCT) to four each Cd-Te and HgTe vibrational modes in the five basic $^{4-n}Cd^nHgTe$ (n=0,1,2,3,4) cells consisting of cations distributed tetrahedrally around a common central Te-anion with mode frequencies determined by the cation configuration of each cell, and oscillator strength reflecting the fraction of cells with that configuration.

In this work FIR reflection spectra of five distinct compositions quaternary solid solutions $Zn_xCd_yHg_{1-x-y}Te$ (ZMCT) are observed. The reflection spectra were obtained by the infrared Fourier spectrometer FTS-14 Digilab in the region 30 to 250 cm^{-1} at 300 K. These spectral curves treated by the Kramers–Kronig (KK) method, give the imaginary part of dielectric functions resolved into the Lorentzian oscillator set. Fig.1 shows the results for sample II of ZMCT (x=0.07,y=0.21) with the following frequencies for Lorentzian oscillators: 108.3 cm^{-1} 112.9cm^{-1}, 116.2 cm^{-1}, 121.0 cm^{-1}, 125.0 cm^{-1}, 131.1 cm^{-1}, 137.3 cm^{-1}, 149.9 cm^{-1}, 160.2 cm^{-1}, 163.5 cm^{-1}, 170.2 cm^{-1}, 179.6 cm^{-1}, 183.4 cm^{-1}, 188.9 cm^{-1}. Part of these lines can be interpreted as Hg-Te–like and Cd-Te–like modes of ternary tetrahedra Hg-Te-Cd (for example 121.0 cm^{-1}, 125.0 cm^{-1}, 131.1 cm^{-1}, 137 cm^{-1}as Hg-Te–like and 149.9 cm^{-1}– as Cd-Te–like); other lines – 160.2 cm^{-1} and 170.2 cm^{-1} - as Cd-Te–like and ZnTe-like modes, respectively, in ternary tetrahedra Zn-Te-Cd [2]; two lines - 116.2 cm^{-1} and 179.6 cm^{-1}- belong to binary HgTe and ZnTe respectively; at last, lines

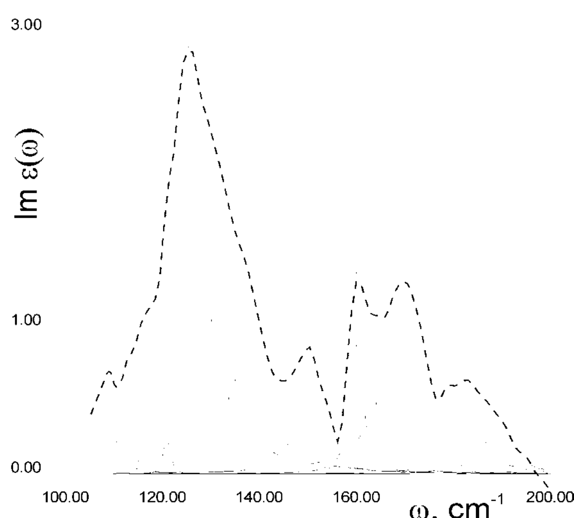

Fig.1. The imaginary part of dielectric function (dashed line) reconstructed by the KK analysis of the experimental reflectivity curve and the Lorencian profiles and fitted curve (continue curves)

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at 108.3 cm^{-1}, 112.9 cm^{-1}, 163.5 cm^{-1}, 183.4 cm^{-1}, 188.9 cm^{-1} may belong to quaternary tetrahedra Hg-Cd-Zn-Te. Generally, 18 lines were distinguished in the FIR spectra of five compositions of ZMCT.

In ZMCT quaternary tetrahedron structures simultaneously coexist several observable configuration tetrahedra: 3 strict-binary (HgTe, CdTe, ZnTe), 9 strict-ternary (three for each of HgCdTe, HgZnTe, CdZnTe), and 3 strict-quaternary ($Hg^2Cd^1Zn^1Te$, $Hg^1Cd^2Zn^1Te$, $Hg^1Cd^1Zn^2Te$). All contribute to increase the number of oscillatory modes to be detected**.** Indeed, the present analysis does show that the analysed quaternary ZMCT has more frequencies of observed spectra and expands the span of frequency region – from 108 to 190 cm^{-1} – respect to ternary solid solutions (118 to 180 cm^{-1}). The oscillator strength of a particular mode enables to define the fraction of cells with each configuration. A detailed analysis is in progress.

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ELECTRICAL CONDUCTIVITY PF BI_2TEO_5 SINGLE CRYSTALS AT HIGH TEMPERATURES

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Bismuth tellurite (Bi_2TeO_5) is a good photorefractive material. It crystallizes in an orthorhombic crystal structure (Abm2) with unit-cell parameters a=11.602 Å, b=16.461 Å and c=5.523 Å. The electrical properties of bismuth tellurite crystals have been studied only below 450 °C and without indicating the ambient atmosphere. In these papers electronic conduction was suggested. In sintered Bi_2O_3-TeO_2 samples, however, oxide ion conductivity was observed at 600 °C. Since the electric properties play a decisive role in the explanation of the photorefractive phenomena, we decided to investigate the electrical conductivity of bismuth tellurite single crystals using impedance spectroscopy and measure the ac and dc conductivity in different ambient atmospheres nearly up to the melting point.

The Bi_2TeO_5 single crystals were grown in our laboratory by the Czochralski method using a high-purity starting material synthesized from the basic oxide components by solid-state reaction. In addition to the undoped samples, Cr-doped crystals were also grown by adding 10^{-3} mol/mol Cr_2O_3 into the melt. The final concentrations were checked by atomic absorption spectroscopy (AAS) after dissolving the samples.

The Complex Impedance Spectroscopic measurements were carried out using a Hewlett-Packard LF Impedance Analyzer (model HP 4192A) in a frequency range of 5 Hz to 13 MHz increasing the frequency in 131 steps. The temperature was varied from 450 °C to 890 °C. The ambient atmosphere was air, oxygen or argon.

The dc conductivity measurements were carried out in vacuum, air or argon using a Keithley programmable electrometer (model 617). The dc conductivity measurement system was interfaced to a 486 PC/AT for automated data acquisition. The applied voltage was 10 V. The temperature could be varied between room temperature and 850 °C with an accuracy of 1 °C. The rate of cooling was 3 °C/min.

The Bi_2TeO_5 single crystals are found to be mixed conductors in which electronic conduction and ionic conduction coexist. The conductivity of the crystals along the [100] direction is much smaller than in directions perpendicular to it. The ambient atmosphere effects the electrical conductivity. The Cr-doping increases the conductivity in the [001] and [010] directions.

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MICROSTRUCTURE AND ELECTRICAL RESISTIVITY OF THE DEFORMED Al - ALLOY

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Electrical resistivity and X-ray diffraction patterns of Al-Mg-Si alloy (used in overhead lines) were measured. The changes of the resistivity of deformed alloy material were observed. The wire deformation was realized with a speed $0.85*10^{-5}$ m/s using INSTRON testing machine. For wire deformation up to about ε=0.5% the decrease of the resistivity measured at both room and liquid nitrogen temperatures was observed. For wire deformation in the range of 0.5% to about 3% the resistivity, after the initial decrease, increased up to the initial value. The authors came to the conclusion that the Al–alloy resistivity behavior corresponds to the processes taking place in alloy microstructure and is connected with effects such as: texture, dislocations, precipitates and microcracks.

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PROPERTIES OF $CoSi_2$ SINGLE CRYSTALS PREPARED BY BRIDGMAN METHOD

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Transition metal silicides have attracted recent attention as model candidates for heteroepitaxial growth on (111)Si, since the structure of the transition metal silicides is almost an ideal match to that of the (111) silicon bulk lattice. Cobalt disilicide ($CoSi_2$) shows a promise for the future devices such as metal base transistors and permeable base transistors. It crystallises in the cubic C1 (CaF_2) type crystal structure, space group Fm3m.

In most cases $CoSi_2$ was obtained only in the form of epitaxial films. Analysis of the Co-Si phase diagram shows that $CoSi_2$ melts congruently at a relatively low temperature of 1326°C. Therefore, it is possible to grow $CoSi_2$ single crystals directly from the melt using Czochralski or Bridgman methods. It is the aim of this work to report results of preparation, microstructure and some physical properties of $CoSi_2$ single crystals.

$CoSi_2$ single crystals were grown by the modified Bridgman method using the vertical induction furnace. Single crystals were grown from a stoichiometric melts in alumina crucibles and in a helium atmosphere. Co (purities: 99.5% and specpure) and Si (purity, 99.999%) were used as the starting materials. The temperature of the charge was measured by means of an optical pyrometer. Crystals were grown at 6 and 12 cm/h. For microstructure and physical properties studies the obtained crystals were cut perpendicular and parallel to their axes by a spark-erosion machine into 1 mm thick plates. Then they were subjected to mechanical and chemical polishing.

The obtained single crystals were studied by X-ray diffraction and photoemission (XPS), SEM and TEM methods, and by the observation of defects after chemical etching. The theoretical and experimental studies have been performed on the electronic structure of $CoSi_2$ crystals. From DC measurements of resistance R in the temperature range 300-4.2K the temperature dependence of resistivity R(T) , residual resistivity ratio RRR and temperature coefficient of resistivity TCR were determined. It was shown that the obtained $CoSi_2$ single crystals exhibit a positive temperature-dependent resistivity and it is a metallic in this temperature range. The room temperature resistivity was 16-18 $\mu\Omega$cm and RRR was 4.2-8.7. Vickers microhardness of $CoSi_2$ single crystals has been also measured. For microhardness measurements a PMT-3 tester with a Vickers diamond indenter was used.

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CHARACTERIZATION OF TiC CRYSTALS OBTAINED FROM Ni AND Cu MELTS

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Titanium carbide (TiC) crystallises in a rocksalt crystal structure, space group Fm3m and has a very high melting point (~3100°C), extreme hardness, high mechanical stiffness and good thermal and electrical conductivity. This makes that it has been widely used in numerous, strategically important, areas of modern technology. For example, very hard titanium carbide particles bonded by metals or steel are unique metal matrix composites (MMC). In recent years there are a number of successful attempts of practical use of [110] TiC single crystals as cold-field electron emitters in electron guns.

The high melting point of TiC makes it difficult to prepare it in a single crystal form. In the last two decades, several authors have prepared TiC crystals by means of Chemical Vapour Deposition (CVD) technique and floating zone, Verneuil and flux/high temperature solutions (HTS) methods. In this studies reported here it was endeavoured to obtain TiC crystals making use of Ni and Cu as high temperature solvents (HTS). So far no microstructure of TiC crystals obtained in this way. This paper fills the gap in this respect and TEM results of microstructure of TiC crystals are presented.

Growth experiments were carried out in a vertical induction furnace. For the starting materials titanium (purity 99.8%), nickel (purity 99.99%), copper (purity 99.995%) and specpure graphite were used. The starting materials were melted in Al_2O_3 crucibles and then soaked at a temperature higher than 1600°C to ensure complete homogeneity and after 2-4 hours the high temperature solutions were slowly cooled down. To reduce the amount of oxide formed, crystallisation processes were carried out in a protective helium atmosphere.

The obtained ingots were metallographically examined using light microscopy, SEM and TEM techniques. Phase composition was determined by the phase analysis method using Inel, Philips and Siemens diffractometers. The presence of Ni, Cu and Ti atoms and their distribution in ingots were examined with an X-ray microanalyser. Thin foil samples, prepared by ionic thinning, were used in electron microscope studies. TEM examinations of thin foils were carried out on a Jeol high-resolution electron microscope JEM 3010. Learning the microstructure of TiC crystals and the Ni and Cu matrices as well as structural identification of the observed phases on the basis of the performed electron diffraction from the studied areas of thin foils were the objective of the study using the TEM method. Using the method of electron energy dispersion (EDS) the analysis of chemical composition was also performed.

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GROWTH AND SPECTROSCOPIC PROPERTIES OF Yb^{3+}:Tm^{3+}:YSGG SINGLE CRYSTAL FIBERS

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The growth of crystal optical fibers is the natural evolution from macroscopic system (bulk crystals) to micro-systems (fibers) and it is aimed to an innovative approach to the development of new laser sources and to study frequency conversion devices. In particular, single crystal fibers doped with Yb^{3+} and Tm^{3+} are very interesting to study the possibility to develop coherent miniature devices for laser operation at 1.5 and 2.3 µm. The interest lies in their possible use in several applications fields, such as medicine and telecommunications. The Yb trivalent ions play a important role: they show a high absorption coefficient in the wavelength region of the high power laser diode around 970 nm and excite the Tm ion manifolds by energy transfer mechanisms.

Single crystals of $Y_3Sc_2Ga_3O_{12}$ have been grown with various levels of doping concentrations (Yb^{3+} and Tm^{3+}) from stoichiometric melts using the micro-pulling-down technique. Growth procedure and peculiarities of the regarded system will be described in detail. We will show optical spectroscopy of samples, in particular absorption and fluorescence.

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THE GROWTH OF Bi AND Ga SUBSTITUTED YIG AND LuIG LAYERS BY LPE METHOD

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Bi substituted Y- and Lu- iron garnets are very good materials for different kinds of magneto-optical applications. In this work we report the preparation of Bi, Ga:YIG and Bi,Ga:LuIG layers on GGG substrates grown by conventional, isotherm dipping LPE technique using $PbO\text{-}Bi_2O_3\text{-}B_2O_3$ system as a solvent. Electron microprobe analysis of the garnet films were performed by energy-dispersive spectrometer and the refractive index of the layers were determined by spectroscopic ellipsometry. The layer growth rate (v_L), saturation magnetisation ($4\pi M_S$) and the Bi content of the layers were determined as a function of the supersaturation of the melt (ΔT) and the substrate rotation rate (ω) at a given melt composition. From these data the $\Delta v_L/\Delta T$, $\Delta 4\pi M_S/\Delta T$, $\Delta 4\pi M_S/\Delta(\omega)^{1/2}$, $\Delta Bi/\Delta T$ and $\Delta Bi/\Delta(\omega)^{1/2}$ growth coefficients were calculated. The physical parameters of the films (thickness, $4\pi M_S$, refractive index, Faraday rotation and the figure of merit) can be very sensitively changed by these growth coefficients. The measured Faraday rotation (Φ) of $Y_{2.5}Bi_{0.5}Fe_{3.8}Ga_{1.2}O_{12}$ and $Lu_2Bi_1Fe_{4.1}Ga_{0.9}O_{12}$ garnet layers with nominal composition are ~ $4.8\ 10^3$ and ~$8.3\ 10^3$deg/cm at 633 nm wavelength, respectively.

Acknowledgments

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OPTICAL INVESTIGATIONS OF $SrLaGa_3O_7:Ho^{3+}$ SINGLE CRYSTALS

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Single crystals of $SrLaGa_3O_7$ doped with trivalent holmium are the promising laser materials in the visible and near infrared parts of the spectrum. The crystals doped with Ho^{3+} at 0.3, 1.5 and 2 at %, respectively, have been grown by the Czochralski method using an iridium crucible and afterheater.

Optical homogeneity and spectroscopic properties of the crystals are of the primary importance in laser and another optical applications. These properties have been measured using an automated spectropolarimeter (600-800 nm) and different spectrophotometers a covering a broad spectrum range (200-3200 nm). These measurements have shown a good to high optical quality of the investigated crystals and their usefulness in laser technique.

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X-RAY PHOTOELECTRON SPECTROSCOPIC STUDIES ON COLORATION OF $SrLaAlO_4$ SINGLE CRYSTALS

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$SrLaAlO_4$ (SLA) single crystals crystallize in the K_2NiF_4-type tetragonal structure (space group I4/mmm) are considered to be suitable for use as high-temperature superconducting (HTSc) thin films substrate because it combines excellent dielectric properties, chemical stability with a good lattice with HTSc. The best quality SLA single crystals were obtained by Czochralski method on a [100] seed but it was noted that the color of the crystals changes from light-yellow to green with changing of growth conditions [1]. The influence of the oxygen partial pressure on coloration of crystal during crystal growth and their spectroscopic properties was reported [2]. Optical investigations on SLA compounds revealed that a change in growth morphology and color of crystals are associated with the nature and distribution of point defects, mainly F-centers. Results of Electron Paramagnetic Spin Resonance (ESR) measurements of $SrLaAlO_4$ crystals showed the presence of 'D' lines changing intensity with the color of the crystals, colorless crystals are much less defective than yellow and green [3].

An investigation of the X-ray photoelectron spectra (XPS spectra) of single crystals of $SrLaAlO_4$ different color is reported. The obtained spectra of Sr, La and Al-ions show no difference while clearly seen difference in the O 1*s* spectra for light-yellow and green crystals was found. O 1*s* spectra of green crystals can be splitted into three superposed spectra. One of the three peaks located at the higher binding energy 531.00 eV was assigned to absorbed oxygen, even though the spectra were obtained from freshly fractured surface. Second peak at 528.91 eV was defined as an oxygen in O1/O2 sites in the unit cell and the last peak at 527.74 eV was considered to be caused by the presence of an interstital oxygen. As for O *1s* spectra for light-yellow crystal, there are only two peaks: first peak at 531.00 eV was reasonably defined as adsorbed oxygen and second peak at 528.85 eV was ascribed as an oxygen of the unit cell.

Results of XPS will be discussed in relation to data of ESR and structure investigations.

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GROWTH OF $GdCa_4O(BO_3)_3$ BY CZ METHOD AND SOME STRUCTURE PROPERTIES

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Recently, $GdCa_4O(BO_3)_3$ (GCOB) single crystal has been reported as an excellent candidate for application in nonlinear optics [1].

In order to reveal the nature and the distribution of defects like inclusions and dislocations crystals were investigated by chemical etching, X-ray methods, transmission electron microscope (TEM) and Raman spectroscopy.

TEM experiments were performed at room temperature with and in general, the crystal is characterized by a regular ordering, however, in some (but rather very few) particles stacking faults perpendicular to the monoclinic b-axis were observed.

The Raman spectra results show that the crystal exhibit low dynamics of molecular and lattice vibrations at room temperature which seems to be a characteristic property of the crystal.

The results of our investigations do not confirm anomalies observed in optical measurements.

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THE INFLUENCE OF THE GROWTH CONDITIONS ON THE ELASTIC PROPERTIES OF $SrLaAlO_4$ AND $SrLaGaO_4$ CRYSTALS STUDIED BY BRILLOUIN SCATTERING METHOD

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The investigated $SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) crystals were grown by Czochralski method at various growing conditions [1]. The light yellow SLA and SLG crystals were grown at the oxygen pressure (in nitrogen atmosphere) of about $4 \cdot 10^{-5}$ atm. The green colour SLA and SLG crystals were obtained at the oxygen pressure higher than $5 \cdot 10^{-3}$ atm [2]. The absorption of the yellow and green SLA and SLG crystals was investigated in the 350 - 700 nm wavelength range. The optical absorption coefficient Δk was calculated in this range. The fundamental absorption edge for green SLA and SLA crystals shifts into the higher wavelength range in comparison with yellow SLA and SLG crystals. It was fond that the colour of crystals is connected with the concentration of the oxygen point defects which can appear in the crystal lattice during the growth process [3-4].

The phase velocities v_i of the longitudinal L and transverse T_2 acoustic waves propagating in the q = [100], q = [101], q = [110] directions of yellow and green SLA and SLG crystals were calculated using Brillouin scattering measurements.

Using the values of the elastic constants C_{ij} of the yellow and green SLA and SLG crystals the linear compressibility coefficient β has been estimated. The character of changes β coefficient for yellow and green SLA and SLG crystals has been discussed in terms of the internal stresses caused by the oxygen point defects appearing during the growth process.

Acknowledgements

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SURFACE STUDY OF THE $Nd_{2-x}Ce_xCuO_{4-y}$ CRYSTAL

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Single crystals of $Nd_{2-x}Ce_xCuO_{4-y}$ (NCCO) were grown by the flux technique in an alumina crucible. The surface morphology was studied using atomic force (AFM), scanning electron microscopy (SEM) with microprobes (EDAX). It was observed that the “as-grown” NCCO single crystals surface is generally flat. Only a few exceptions were detected. Among them there were steps of the height of about five and nine multiple of the lattice parameter ***c***. Interesting nanocaves that appeared as a result of flux drops penetration are presented. Influence of the flux growth technique and reducing process on the surface morphology is widely discussed.

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GROWTH AND ELECTRIC TRANSPORT OF CA-DOPED $PrBa_2Cu_3O_{7-}$ SINGLE CRYSTALS

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Crystal growth of Ca-doped $PrBa_2Cu_3O_{7-\delta}$ (Pr-123) single crystals by slow cooling of Pr_3O_{11}-$CaCO_3$-$BaCO_3$-CuO melts (self-flux technique) in ambient air atmosphere was studied. As the first approach the growth of Ca-free crystals in Al_2O_3 and ZrO_2 crucibles was investigated. The best quality crystals with the average size of 5 x 5 x 0.2 mm^3 were obtained from Al_2O_3 crucibles for Ba/Cu = 0.41 and 15 wt.% (2.41 mol.%) of stoichiometric Pr-123 solute in the melt. Next, using $CaCO_3$ as calcium source (0.09-12.68 wt.%), the good quality $Pr_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ crystals with $0 \le x \le 0.26$ were grown in the Al_2O_3 crucibles from the solution with fixed value of Ba/Cu = 0.41. The oxygenated single crystals with size up to 5 x 8 x 0.2 mm^3 were used for electric transport investigations from four-probe resistivity measurements. The temperature dependence of resistivity of Ca-doped Pr-123 crystals is typical for systems with locallized states and, in principle, follows the Mott law for variable-range hopping (VRH).

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CRYSTAL GROWTH AND OPTICAL PROPERTIES OF $LaGaO_3/SrTiO_3$ MIXED CRYSTALS

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A series of $La_{1-x}Sr_xGa_{1-x}Ti_xO_3$ solid solution single crystals with x = 0, 0.04, 0.08 and 0.12 were grown by the Czochralski method with x = 0.01, by the floating zone method. The crystals were grown from the melt with stoichiometric Ga_2O_3 amount at a growth rate ranging from 2.5mm/h for pure $LaGaO_3$ to 1.2mm/h for x = 0.08. Large good quality single crystals were grown by the Czochralski method in the concentration range from 0 to 0.04. Thermal analysis proved that the temperature of the first order phase transition observed in pure $LaGaO_3$ at 150°C falls to 76°C at x=0.04 and remains almost constant at higher x.

In the absorption spectrum of the crystal there was stated the presence of Ti^{3+} ions beside Ti^{4+}. Ti^{3+} ions arises due to some reducing conditions of the crystal growth. It was found that electron delocalization at higher temperature, eg. in oxidation-reduction reaction: $Ti^{4+} + e = Ti^{3+}$ may appear in optical spectra as charge transfer bands in the NIR region giving rise to blue absorption. The observed fluorescence of ^2E - $^2T_2$ transition of Ti^{3+} in the crystals shows two bands centered at about 420 and 447 nm coming from excitation at 314, 340 and 384 nm, which suggest tetrahedral coordination of Ti^{3+} ions (may be interstitial) whilst Ti^{4+} ions enter to the crystal at octahedral positions of Ga. The fluorescence spectra are strongly polarized.

The goal of the present work is to examine growth conditions, optical spectra and potential emission characteristics of Ti doped $LaGaO_3/SrTiO_3$ mixed crystal, which may be of interest for practical laser application. We analyze also the influence of annealing in oxidizing and reducing atmospheres and γ-irradiation treatments on optical properties of Ti doped $LaGaO_3/SrTiO_3$ mixed crystals.

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STRUCTURE OF $NaNbO_3$: x Mn SINGLE CRYSTALS AT ROOM TEMPERATURE

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A series of $NaNbO_3$:Mn single crystals had been obtained from flux by double crystallisation. Manganese oxide was introduced to melted sodium niobate to obtain a nominal Mn content within 10%mol [1]. The XPS made at room temperature allow to determine that real concentration of Mn dopant is about one order lower. Solubility limit was estimated as ≈1%wt. It was concluded from valence band analysis that Mn ions built in niobium sublattice mainly [2].

DTA test was performed in the range 300-700K. All the samples shoved a sharp peak connected to structural antiferroelectric phase transition known from pure sodium niobate. The phase transition temperature lowers, while the real concentration of Mn increases, with the rate –15K/%wt(Mn). One can deduce that crystal symmetry and sequence of phases remains essentially unchanged within the investigated range of Mn concentration and temperature interval.

The X-ray spectrum was recorded at room temperature. This spectrum can be generated for perovskite $NaNbO_3$ when orthorhombic Pbcm space group is chosen for simulation.

The pseudo-perovskite unit cell shoves monoclinic distortion, $\beta \neq 90°$ [3] [4] [5]. The evolution of lattice constants with Mn concentration change was examined.

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GROWTH AND X – RAY TOPOGRAPHY OF $ScFe_4Al_8$ SINGLE CRYSTALS

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There is a large family of the tetragonal RT_4M_{12-x} compounds, where R is rare earth or actinide element, with $ThMn_{12}$ type structure. These materials are formed in principle as ternaries and they can be divided into two distinct subgroups: the first one with high concentration of transition element T and the second one with lower concentration of T ranging from x = 4 to 6. The representatives of the first group are potential interesting magnetic materials, whereas the members of the second group, $ScFe_4Al_8$ among them, exhibit puzzling physical properties. In this compound there are four nonequivalent crystallographic positions: the (a) position occupied by the Sc atoms, the (f) site occupied by the Fe atoms, and the Al atoms are located in the (i) and (j) sites. For determination of physical properties one needs single crystalline material. These single crystals were obtained by Czochralski method from a levitated melt. The X – ray Berg – Barrett topography exhibit that the obtained single crystals were a good quality.

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CRYSTALLIZATION OF $Bi_2Sr_2Cu_1O_6$ AND $Bi_2Sr_2Ca_1Cu_2O_8$ PHASES IN Bi-Sr-Ca-Cu-O GLASS

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It is now well known that glass in Bi-Sr-Ca-Cu-O system is converted into high-T_c superconductors after proper annealing [1,2]. This preparation technique is very attractive because of possibility of producing superconducting fibres. Among all the types of glasses from this system, the $Bi_4Sr_3Ca_3Cu_4O_x$ (4334-glass) glass is a very important one. It is because this glass can be converted into $Bi_2Sr_2Cu_1O_6$ (2201-phase) with $T_c \approx 20$ K, $Bi_2Sr_2Ca_1Cu_2O_8$ (2212-phase) with $T_c \approx 85$ K or $Bi_2Sr_2Ca_2Cu_3O_{10}$ superconducting phase (2223-phase) with $T_c \approx 110$ K.

In this paper we report crystallization of 4334 glass at 472°C and 800°C for the different time of annealing. The samples were studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), differential scanning calorimetry (DSC), termogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). Crystallization at the temperature 472°C leads to the formation of 2201-phase (metallic or superconducting). This phase forms some granular structure with randomly distributed grains in glassy matrix. For the time of heat treatment longer than 100h, the mean size of grains was about 100 Å. We found that oxygen needed for crystallization of 2201-phase is taken from glassy matrix and the change of valency state of copper ions $Cu^{+1} \rightarrow Cu^{2+}$ is observed. Annealing at 800ºC gives mainly 2212 phase, but during crystallization process also some other phases grow. After 200h of heat treatment at this temperature, we have also observed 2201-phase, 2223-phase and Cu_2O.

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EPR STUDY OF THE NATURE OF INCORPORATION SITES OF Mn(II) AND Fe(III) IONS IN AMMONIUM OXALATE MONOHYDRATESINGLE CRYSTALS GROWN FROM AQUEOUS SOLUTIONS

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It is well known that impurities present in a growth medium influence the growth kinetics, the morphology and the quality of crystals. One of the parameters determining the quality of crystals growing from growth media containing impurities is their segregation coefficient. The value of the segregation coefficient during crystal growth from solutions depends on a number of factors like solution supersaturation, growth temperature, impurity concentration in the medium and nature of the impurity. It is these very factors which determine the growth kinetics of a crystal growing from solutions. Consequently, there is an increasing interest in the investigation of the relationship between the effects of ionic impurities on the growth kinetics and the value of their segregation coefficient in crystals growing from aqueous solutions.

Among the various impurities, transition metal ions are of particular interest because they lead to changes in the properties of a crystal by affecting the symmetry and the bonds in the crystal lattice. EPR spectroscopy is a powerful tool to investigate these changes. In principle, an EPR spectrum may be obtained for any system, such as Cu(II), Ni(II), Mn(II), Fe(III) and Cr(III) ions, with an odd number of electrons with spin S = 1/2, 3/2 or 5/2. In this work the results of a preliminary EPR study of the nature of incorporation of Mn(II) and Fe(III) ions in ammonium oxalate monohydrate single crystals grown on seeds from aqueous solutions at a constant temperature, solution supersaturation and impurity concentration are described and discussed.

The EPR spectra of ammonium oxalate single crystals doped with Fe(III) and Mn(II) ions were recorded at room temperature. Every EPR spectrum with Mn(II) ions revealed two sets of Mn(II) ions occurring in five sextets of lines (S = 5/2 and I = 5/2, d^5 configuration). One broad line corresponding to Fe(III) ions was observed only in the spectra of the crystals rotating in the *a-c* and *b-c* planes with g = 2.196. When the Fe(III) concentration is lower in the growth solution, this line is invisible. The spectra of Fe(III) are isotropic in all crystal orientations. At least two physically nonequivalent complexes of Mn(II) and Fe(III) ions are observed. An detailed analysis of the angular dependence of the EPR spectra for Mn(II) ions was performed. The anisotropy of the spectra of both type of complexes show different behaviour. The analysis indicated an orthorhombic symmetry of the Mn(II) ions positions in the crystal lattice.

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COORDINATION GEOMETRIES OF THE METAL IONS IN THE METATALLOPHTHALCYANINATO COMPLEXES

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Numerous applications of metallophthalocyaninato complexes in a wide range of life areas causes great interest in their syntheses, technology and coordination chemistry. The metallophthalocyaninato complexes are coordination compounds in which the metal ion M^{n+} of charge $1 \leq n \leq 6$ is encompassed by one or two negatively charged tetraisoindole ligands yielding mono or diphthalocyaninato complexes. Besides these two types metallophthalocyaninato complexes the homoleptic triple-decker phthalocyaninato complexes in which two trivalent metal ions are stapled by three phthalocyaninato(2-) ligands and the dimetallophthalocyaninato complexes in which the one phthalocyaninato dianion coordinates two M^{+} ions have been known. Additionally a very distinct class of metallophthalocyaninato complexes, the bicyclic phthalocyanines have been also obtained. In contrast to the normal phthalocyaninato(2-) complexes, the phthalocyaninato(2-) ligand consists of four isoindole rings which are bridged by azamethine nitrogen atoms, the bicyclic phthalocyaninato ligand consists of six isoindole moieties

The geometry of the metal ions in the metallophthalocyaninato complexes is detenoined by (1) the basic factors of the phthalocyaninato macroring such as the diameter of the hole, relatively inflexible skeleton, anionic charge and aromaticity as well as by (2) the oxidation state and the effective radius of the metal M^{n+} ions Additionally it should be stated that the stoichiometries and the geometries of the metallophthalocyaninato complexes depends also on the conditions of the reaction syntheses, since many metallophthalocyanines may be redox active, in which the metal ion and/or phthalocyaninato ring change the oxidation state what usually leads to the changing of the stoichiometries and/or geometries ofmetallophthalocyaninato complexes.

A short summarizing of various types of metallophthalocyaninato complexes focused mainly on the complexes obtained and characterized in our laboratory will be presented

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HYDROXYAPATITE PRECIPITATION IN A SEMIBATCH PROCESS

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Hydroxyapatite (HA) is an important biomaterial, with also others applications as catalyst, in chromatography or gas sensor. Its synthetic obtention is based on precipitation techniques. Some studies have been reported using batch and continuous reactors [1,2]. In this work a precipitation study of HA in aqueous solution and using a semibatch process is presented. The influence of pH, reactant addition and flow rate on the characteristics of the obtained product, as stoichiometry and crystallinity, is analysed.

Experiments have been done in a thermostatized reactor at 85ºC, with agitation under nitrogen atmosphere and controlling pH with a pH-stat equipment. The chemicals were $CaCl_2 \cdot 2H_2O$ and K_2HPO_4 analytical grade, and doubly destilled water. The flow rate of reactant addition has been controlled with a peristaltic pump. The products have been characterized by IR spectroscopy and X-ray diffraction; the stoichiometry, or Ca/P ratio, has been determined by induced coupled plasma atomic absorption AA-ICP.

The mixing process determines the stoichiometry of the precipitate, which also shows a good crystallinity. The crystals present nanometric sizes, which have been stimated from the Scherrer equation and confirmed by SEM images. The addition of phosphate over calcium leads to a stoichiometric HA (Ca/P=1.67) with a good crystallinity since the beginning of the process, meanwhile the addition of calcium over phosphate leads to a non-stoichiometric HA which is calcium defficient (Ca/P=1.53); in the later, the ignition of the precipitates gives HA and β-TCP. There is no effect of pH in the range between 8 and 9, but the system is better controlled at pH=9. Higher flow rates, in the studied range, don't change the characteristics of the product, but reduces the synthesis time, increasing the industrial interest of the method.

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CRYSTAL SIZE DISTRIBUTION IN HYDROXYAPATITE PRECIPITATION IN A MSMPR REACTOR

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The synthesis of hydroxyapatite (HA) powders with controlled characteristics of morphology, stoichiometry, crystallinity and crystal size distribution (CSD) is important in medicine and materials science. Well characterized stoichiometric HA powders using a continuous flow MSMPR reactor have been obtained [1]. The aim of this work is to study the kinetics of crystallization by the analysis of the CSD using the method of moments, and discussing the mechanism of particle formation.

The experimental set-up was composed by a continuous flow MSMPR reactor, two feeding tanks with $CaCl_2$ and K_2HPO_4 solutions, a peristaltic multichannel pump, a pH-stat apparatus and a thermostat. Experiments were performed at two residence times of 30 and 60 minutes, pH=9 and 85ºC. The CSD was determined with a Coulter LS particle size analyzer, being the instrument range between 0.1 and 1000 μm.

The method of moments in crystal volume coordinates, supposing a nucleation-growth-agglomeration mechanism for particle formation, has been used to solve the population balance equation and to calculate the kinetic rates. The rates of nucleation and growth (B^o and G_v) and the agglomeration kernels (β) vary in the intervals: $B^o=10^{10} - 10^{12}$ dm^{-3} s^{-1}, $G_v = 10^{-21} - 10^{-22}$ m^3 s^{-1} and $\beta=10^{-13} - 10^{-15}$ dm^3 s^{-1}. The only clear observed correlation relates the decrease of G_v and β with the rise in the residence time. The incresase in feeding reactants concentration seems to decrease the values of β, fact that could be attributed to the breakage of agglomerates with the increase in the suspension density.

The analysis of the CSD by the plots ln[n(v)] versus volumen v, shows an initial rise from v=0.01 to 0.1 μm^3, followed by a decrease with a deviation from linearity and some minor maxima. This analysis suggests that the mechanism of particle formation consists of nucleation, ordered aggregation of elemental nanocrystals with some crystal growth, at a constant residual supersaturation, acting as cementing mechanism inside the aggregates.

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THE INTERFACIAL TENSION FOR SOME MOLECULAR CRYSTAL – NONELECTROLYTE SOLUTION SYSTEMS ESTIMATED FROM INDUCTION TIME, SURFACE TENSION AND SOLUBILITY DATA

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Crystallization of chemical compounds from solutions is an important separation – purification process with increasing industrial application potential, especially in the organic chemical industry. It is also very important for the production of highly perfect organic crystals, creating possibility of their growth at or near room temperature, development of their natural faces and elimination of stress and strains problems resulting from inhomogeneous contraction of the ampoule or support material and adhering crystal.

One of the most important parameters that enabled description of both nucleation and growth of such obtaining crystals is an interfacial surface tension, appearing in practically all theoretical expressions describing the rates of these processes. Since generally there exist not experimental techniques to measure this parameter, therefore, it is necessary to estimate its value for arbitrary systems.

In our work we present results of the interfacial tension estimation from measured by us induction time, surface tension and the solubility data for naphthalene, acenaphthene and fluoranthene in 1,2-dichloroethane.

In the present work we have observed that the interfacial tension values, estimated on the basis of the induction time are lower than those obtained from the solubility data, however, they are of the same order of 10^{-2}J/m^2.

Moreover, we have also found that the surface tension measured for the investigated solutions by the stalagmometry method, correlates well with the above interfacial tension values, and especially with those calculated from solubility data; namely these latter are almost strictly twice higher than the values of surface tension.

Thus, for nonelectrolyte solutions with regular behavior, such as those investigated here, the relatively easy to perform stalagmometry measurements may be useful in estimation of the interfacial tension, a value which practically cannot be measured by experiment.

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THE METASTABLE ZONE WIDTH OF SOME GROWTH SOLUTIONS OF FLUORANTHENE WITH REGULAR BEHAVIOR

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Aromatic hydrocarbon fluoranthene ($C_{16}H_{10}$) is typical representative of organic photoconductors and scintillators.

Due to interesting luminescent properties this compound is often used as a dopant of molecular crystals, prepared for laser spectroscopy.

A considerable thermal stability of fluoranthene allowing purification by zone refining causes simultaneously that its high purity crystals may be grown from the melt, from the vapor and from the solution.

The outstanding features of solution growth are:

I. Growth at or near room temperature,
II. Bulk crystals of relatively highest perfection,
III. Development of natural faces with possibility of intended modification of crystal morphology, depending on the solvent.

Knowledge of the metastable zone width, which generally defines an ability of the growth solution to supersaturation or supercooling, is very important for the design and control of crystals growth from solutions.

The maximum supercooling ($\Delta\Theta_{max}$), which is usually taken as a measure of the width of this zone has been determined experimentally for fluoranthene in trichloroethylene and 1,2-dichloroethane, on the basis of temperature dependencies of ultrasonic waves velocity. These dependencies were measured using a microprocessor apparatus, adopted specially for easily volatile organic solvents.

Parallel assessments by other authors have shown this parameter to be related to the cooling rate *b* by the expression:

$$\log b = (m-1) \log (dc^*/dT) + \log k_n + m \log (\Delta\Theta_{max})$$

where k_n is the rate constant for nucleation and dc^*/dT is the rate of change of solubility with temperature. Thus a linear relationship should exist between log *b* and $\Delta\Theta_{max}$, the slope *m* of which is defined as the order of the nucleation process.

The estimated data for five different cooling rates have confirmed the above equation; the logarithmic dependencies between $\Delta\Theta_{max}$ and *b* were linear for both investigated solutions. Moreover, we have found that the values of supercooling increase with the cooling rate, and the order of nucleation is dependent on concentration of solutions.

It has also found that the investigated solutions are nonideal with positive deviations from the ideal solubility of fluoranthene and moreover, they may be treated as regular ones.

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ELECTROMAGNETIC INTERACTION OF DYE-SOLVENT MIXTURE

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In this paper the description of dynamics of the electromagnetic fields in the dye-solvent mixture in the concept of extended phenomenological electrodynamics is presented. For the description of the structure of material a phenomenological model of the multicomponent body is used. Such a model is based on the following assumptions:

1. a body consists of many homogeneously (ideally mixed) different components and
2. all components are located in each space point occupied by the body.

It seems that the dye-solvent mixture fulfils above phenomenological supposition for the multicomponent body. Dynamics of the electromagnetic field has been expressed in the Lagrange – Hamiltonian formalism, and can be used in investigation of the local electromagnetic field in the dye – solvent mixture. Such a study may be important for a photoelectrochemical cell with organic dye dissolved in liquid matrix (liquid polymer or liquid crystal) in which solar energy can be converted into electric energy.

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KINETICS OF PROTEIN CRYSTAL GROWTH IN MASS-CONVECTION REGIME

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We present a study, based on experimentally motivated assumption, that the process of protein crystallization (e.g., that of lysozyme) is realized in a mass-convection manner, than being driven by diffusion. Next, we assume, that the mass conservation law is being fulfilled, and that the attractive potential is of (screened) electrostatic nature. A role of the double-layer, surrounding the crystal under growth is indicated, and thermodynamic conditions, responsible for association of protein "over-ions" to a growing and charged nucleus are carefully specified. Moreover, there is a possibility to take into account the hydrophobic effect clearly present in the electrolyte. We are also able to examine a role of fluctuations in the studied process, which makes our study closer to reality.

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SIZE OF GROWTH UNITS OF AMMONIUM OXALATE MONOHYDRATE SINGLE CRYSTALS DEDUCED FROM EXPERIMENTAL DATA ON THE VISCOSITY OF SUPERSATURATED AQUEOUS SOLUTIONS

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The theories of crystal growth are based on the postulate that growth units present in a growth medium in the form of atoms or molecules and they are incorporated in kink sites present in the ledges produced on flat faces appearing in the growth habit of the crystal. Analysis of the growth morphology of crystals in terms of connected nets, on the other hand, suggests that the growth units are relatively large of the order of the unit cell of the crystal or its part [1]. A survey of the growth kinetics of crystals of electrolytes and macromolecules grown from solutions from the standpoint of the surface diffusion model of crystal growth, proposed by Burton, Cabrera and Frank, revealed [2] that different dimensions of growth units integrating into kinks provide a better picture of growth kinetics and satisfactorily explain deviations from the predictions of the classical theory. In view of these facts as well as our poor knowledge of the nature of growth units it is of interest to search for experimental and theoretical methods that enable one obtain information about the dimensions of growth units present in supersaturated media.

In this presentation the results of a study of the size of growth units present in supersaturated aqueous solutions of ammonium oxalate monohydrate (AO) from experimental data of their viscosity measured in the temperature range between 25°C and 47°C and supersaturations between about 10% and those corresponding to three-dimensional nucleation are presented. The experimental data were subsequently analysed using the theoretical models advanced by Einstein, Vand, Jones and Dole, and by Goldsack and Franchetto. It was found that the expressions of the dependence, given by Einstein and by Goldsack and Franchetto, between the ratio of the viscosities of supersaturated solution and pure water on solute concentration describe the data most satisfactorily while the Jones-Dole equation yielded the worst fit. The value of the radius of species present in the solutions predicted by different models was found to lie between 0.30 and 0.47 nm while the B coefficient of the Jones-Doles equation is 0.55 dm^3/mol. The estimated dimensions of the species relatively large and lie between the values of 0.3 nm and 1.2 nm of the lattice parameters of AO crystals. The large dimensions of the species in saturated solutions also suggest that they are structure makers in the solution. The value of the activation energy E in the Goldsack-Franchetto relation depends on both solution concentration x and temperature T and is equal to $0.0287RT/x$ (where R is the gas constant, and x is expressed in molar fraction and T in Kelvin). For typical values of T = 300 K and x = 0.01 one obtains E = 7 kJ/mol, a value close to the activation energy for viscous flow.

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ON THE EFFECT 0F CU(II) IMPURITY ON THE GROWTH KINETICS OF AMMONIUM OXALATE MONOHYDRATE SINGLE CRYSTALS FROM AQUEOUS SOLUTIONS

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It is well known that at a given supersaturation σ impurities often lead to a decrease in the growth rate R of a face. The dependence of R on impurity concentration c_i is usually explained in terms of models of adsorption of impurities at kinks in step ledges and at the surface terrace on the F faces of single crystals. However, in some cases it is found that the rate initially increases and then decreases with increasing c_i, thus exhibiting a peak at some c_i. The initial increase in the growth rate has been attributed to a decrease in the surface free energy as a result of adsorption of impurity particles on the growing surface.

In this paper the effect of concentration of Cu(II) ions and solution supersaturation on growth rates along <100>, <010> and <001> directions [corresponding to (100), (010) and (001) faces] of ammonium oxalate monohydrate (AO) single crystals is studied 30°C and supersaturations up to 10%. Instead of analysing the dependence of face growth rates R on impurity concentration c_i for different supersaturations σ in terms of Cabrera-Vermilyea and Kubota-Mullin models, the dependence of R on σ for different c_i were analysed using spiral growth theory involving cooperating dislocation source and multiple nucleation model .

It was observed that the growth rates of the (001) face of the crystals decrease while those of the (100) and (010) faces increase with an increase in the concentration of an impurity, and that both the cooperating screw dislocation and multiple nucleation models describe the experimental data on growth kinetics from pure and impure solutions satisfactorily. Analysis of the data according to these models revealed that an increase in the face growth rate with impurity concentration is associated with a decrease in the free energy of the growing face (thermodynamic effect) while a decrease in face growth rate with an increase in the concentration of the impurity is a kinetic effect involving a reduction in the value of the kinetic coefficient β for the motion of steps on the surface. It is also found that usually both effects take place simultaneously but one of them dominates during the growth of a face. The dependences of surface free energy and kinetic coefficient on impurity concentration follow Freundlich adsorption isotherm.

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SURFACE MORPHOLOGY OF THE {010} CLEAVAGE FACES OF POTASSIUM HYDROGEN PHTHALATE SINGLE CRYSTALS

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Many interesting phenomena connected with the crystal structure can be investigated on the cleaving surfaces of ionic single crystals. Among the ionic crystals, potassium hydrogen phthalate (KAP) is an attractive material and several papers [1,2] have been devoted to the study of its growth, morphology and etching behaviour. This crystal has a perfect {010} cleavage plane. However, until now the surface morphology of the cleavage faces of the crystal has not been investigated. In this work are described and discussed some preliminary results of the nature and morphology of the {010} freshly cleaved surfaces of potassium hydrogen phthalate (KAP) crystals grown from aqueous solutions studied by optical and atomic force microscopy.

Among the common features observed on the {010} cleavage surfaces of KAP crystals are elementary steps with height 1.386 nm equal to the lattice parameter *b* (elementary steps) and multilayer steps with heights equal to twice and several times the height of *b* the elementary steps. It was found that the elementary steps often produce V-shaped patterns composed of two steps one of which is oriented along a low-index direction while the other is oriented roughly along the direction of crack propagation. The multilayer steps seems to arrange along different directions. Large areas without any steps were also observed.

The occurrence of an easy cleavage along {010} plane of the KAP crystals is a consequence of weak Van der Waals type of bonds between the neighbouring sheets of planes. The weak bonds between the {010} planes is also responsible for relatively large areas completely free of the cleavage steps. The observations of the orientations of elementary steps along low-index directions and the formation of V-shaped structures are similar to those observed on the cleavage faces of L-arginine phosphate monohydrate [3] and potassium bichromate single crystals [4]. Analysis of the results showed that the directions of elementary steps correspond to the directions of strong connected nets (i.e. PBCs) on the face while the formation of V-shaped structures is associated with the cutting of dislocations loops by a moving crack front.

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NMR INVESTIGATION OF NATROLITE STRUCTURE

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The mineral natrolite ($Na_2Al_2Si_3O_{10}2H_2O$) is the typical channel-type compound with porous structure (zeolite). The natrolite unit cell is orthorhombic with space group *Fdd2*. The natrolite aluminosilicate framework contains AlO_4 and SiO_4 tetraedra, bonded via common oxygen atoms. The water molecules are situated at regular positions within the channels and form hydrogen bonds to oxygen's atoms of the aluminosilicate structure. The sodium ions are situated at regular positions within the channels also.

In this study we have undertaken a detailed investigation of natrolite structure by Nuclear Magnetic Resonance (NMR) of ^{1}H, ^{23}Na and ^{27}Al nuclei. From the temperature dependencies of the NMR spectra of ^{1}H nuclei it follows that there are two different kinds of the water molecular motion. The molecular motion of the first kind is the 180^0 flip motion and second one is the diffusion of the water molecules. From NMR data it follows that water molecules diffuse along the vacancies whose positions coincide with the regular positions of water molecules. From the temperature dependencies of the NMR spectra of ^{23}Na and ^{27}Al nuclei it follows that observed transformations of NMR spectra are concerned with the diffusion of the water molecules and with the dehydration of water molecules. The obtained results have been compared with results published early [1-13].

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SOME PROPERTIES OF QUATERNARY $Mn_xCd_yHg_{1-x-y}Te$ MONOCRYSTALS

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Investigation of Mn_xCd_y $Hg_{1-x-y}Te$ monocrystals with x in the range $0.05<x<0.15$ and $0.1<y<0.25$, obtained by modificated Bridgment method was carry out. The temperature dependence of Hall constans and conductivity in the temperature range 77K - 300K were measured. The magnetophonon resonance was investigated on samples with the high carrier mobility.

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STUDY OF THIN GOLD FILMS SURFACES IN DIFFERENT STAGES OF FORMATION

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The aim of the paper is to research an influence of time of evaporation on surface structure and morphology of very thin gold films. The studied films were deposited on glass substrate under UHV conditions (10^{-10} Torr). By changing the time of the deposition from 2 to 50 minutes various Au structures and thin films were obtained, namely, isolated gold islands lower than 20 nm, discontinuous films with a nanometric structure, and continuous films of the thickness of about 50 nm. The film surfaces were investigated by means of two complementary methods, the grazing incidence X-ray reflectometry (GIXR), and the atomic force microscopy (AFM). The X-ray measurements were performed by using a Philips high-resolution diffractometer. The results were interpreted basing on the Fresnel theory. The RMS values of the surface roughness determined by GIXR method are equal to 1.2 nm, 1.0 nm, and 0.7 nm, respectively.

The morphology of the surfaces was investigated by means of the atomic force microscopy in contact (repulsive), and constant force modes under ambient conditions, using a commercial instrument, model TMX 2000 'Discoverer' (TopoMetrix, CA).
A good agreement of the results of both methods was achieved.

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MICROSTRUCTURES OF INHOMOGENEOUS, DISCONTINUOUS METAL FILMS – THE COMPUTER SIMULATIONS AND STATISTICAL DESCRIPTION

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The ranges of statistical description of the systems may be determined on the basis of inverse power law (Mandelbrot law). The slope of the straight line representing the power law in a double–logarithmic plot, determined as ($-1/\mu$) (μ being a critical exponent), characterizes the distribution of elements in the microstructure. For $\mu > 2$ two parameters of distribution (the mean value and the variance) are finite, Gaussian or log-normal distribution describes the system. When $1<\mu<2$ only the mean value is finite. Therefore, for a description of such system, a statistical distribution with one parameter may be used. For $\mu<1$, both the mean value and the variance are infinite. The objects of such microstructure are distributed according to the Lévy stable distribution.

In this paper the inverse power law is used to describe the microstructure and the statistical distribution of discontinuous metal films on dielectric substrates for $2<\mu$ (second and threeth case).

The inhomogeneous films were obtained experimentally and using the computer simulations. The ranges of critical exponent μ, for which the Poisson, Lévy or Pareto's distribution describes the microstructures were determined. The statistics determined on the basis of microscopic examination is compared with that for the simulated microstructure.

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ELECTRICAL CONDUCTION MECHANISMS IN DISCONTINUOUS Pt FILMS

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Electrical properties of Pt discontinuous films were investigated. Pt films with different coverage coefficients (p) were evaporated onto quartz-glass substrates under vacuum conditions ($p=3\ 10^{-6}$Torr) The temperature dependencies of resistance measured in vacuo in situ made possible to determine activation energy of resistance for the films. These values of activation energy were compared with those obtained on the basis of structural examinations conducted bay means of electron microscope. The dependencies of the island diameters and of the gaps on coverage coefficient were determined for examined films. The resistance of Pt – films versus coverage coefficient was also presented in semi-logarithmic scale. It has been found that the electrical properties of the film are subject to significant change near the percolation threshold. This behaviour is to be attributed to a change in the type of conduction. Films with coverage coefficient $p<p_c$ (p_c – critical coverage coefficient) exhibit high resistance, their activation energies of resistance are smaller then zero. For $p>p_c$ the resistances reach lower values, the activation energies of resistance are greater then zero. The conduction mechanisms in discontinuous Pt films are proposed.

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TUNNELING STUDY OF FERROMAGNETIC NI CLUSTRES

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This paper presents results of our experimental investigations of Ni clusters deposited on *ab* surface of $Bi_2Sr_2CaCu_2O_{8+y}$ (Bi2212) single crystal and on highly oriented pyrolytic graphite (HOPG). Samples were carefully selected for their smooth and uniform surface. Their layered crystalline structure allows one to prepare an atomically flat surface by cleaving.

Clusters were deposited on fresh cleaved in ultra-high vacuum *ab* plane of Bi2212 or HOPG substrates. The ferromagnetic clusters of the diameter 10 to 15 nm were created in the gas plasma condensation or evaporator with integral flux monitor. The tip was constructed from Pt-Ir wire (0.5 mm diameter) and prepared by electrochemical etching/polishing in KOH solution.

The most popular approach to study the local density of states (LDOS) is scanning tunneling spectroscopy (STS). The scanning tunneling spectroscopy was performed at 24K and room temperature. The spectra measured above the Ni clusters and directly above the substrate reveal remarkable differences. Combined scanning tunneling microscopy and scanning tunneling spectroscopy (STM/STS) studies provide useful information about the relationship between topography and the local electronic structure.

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STRUCTURE OF Ge-BASED FILMS EXHIBITING THERMOELECTRIC EFFECT

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We have fabricated and characterized thin films of Ge doped with various components (B, Au, Sb) in order to produce the resistive films (below 1 Kohm/□) with useful Seebeck effect. The Ge-Me thin films of 0.7-3 μm thick were deposited by magnetron method. The 10 cm circular targets with separated zones of individual components were used. The targets were supplied with constant or unipolar pulsed voltage of 160 kHz. The films condensed on various substrates (Corning 7059 glass, fused, quartz, ST-50, D263 Schott foil glass) at the temperatures between 360 and 1040 K. The structure and phase composition of films were determined by X-ray and ED diffraction methods. The amount of the dopant in the sputtered films was controlled by X-ray microprobe analyzer. The surface topography of the films was examined by SEM investigations. These studies indicate a complex structure of as-sputtered films. The films are composed of amorphous or crystalline matrix of Ge that includes microcrystallites of phases of metals which were introduced during sputtering. The amorphous as-sputtered films convert into polycrystalline films during thermal treatment in vacuum at above 723 K.

The presented results for magnetron sputtering of Ge films doped with B, Au and Sb allow to estimate the significance of particular parameters of deposition process in evaluation of structural properties. It was shown that the level of power, substrate temperature during deposition or post-annealing and dopant concentration have a considerable influence on the crystallite size and preferred orientation of cubic structure of diamond type of Ge.

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TRANSPORT PHENOMENA IN GERMANIUM FILMS USED AS SENSITIVE MATERIAL FOR CRYOGENIC RESISTANCE THERMOMETERS

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Ge films on GaAs are very promising sensitive material for cryogenic thermometry. Several types of wide-range cryogenic resistance thermometers based on Ge films have been developed and produced. They cover temperature range for operation from 0.1 to 500 K.

This paper deals with study of transport phenomena in germanium films, which are responsible for the magneto and thermosensitivity in the temperature range from 1.5 to 400 K and in magnetic field up to 14 T. We present and analyze the investigation of Hall effect, magneto-resistance and electrical conductivity for different Ge films.

Mechanism of electrical conductivity in Ge films essentially depends on the temperature range studied, as well as films growth conditions. Technological conditions of Ge/GaAs heterostructure formation determine the level of doping and compensation degree, as well as the degree of structure perfection of the Ge films.

At sufficiently high temperature range the thermoemission from Fermi level into percolation level are observed in heavily doped and compensated films.

At low temperature the hopping conductivity through the localised states prevails. From analysis of the temperature dependence of resistance we can conclude that the Ge film conductivity does not obey an exponential law with constant activation energy at low temperatures. The dependence of conductivity on the temperature can be described by the variable-range hopping. Such variable-range hopping conductivity may correspond to the Shklovskii or the Mott models depending on technological conditions of film formation. Depending on film growth conditions, low-temperature magneto-resistance of the Ge films can be positive and negative. It corresponds to different mechanisms of low-temperature electrical conductivity.

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CHEMICAL VAPOR DEPOSITION OF DIAMOND FILMS IN HOT FILAMENT REACTOR

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Polycrystalline diamond film growth on a silicon substrate has been a matter of a great interest due to potential application of films in microelectronics and optics. For this purpose it is important to determine the optimal experimental conditions for obtaining high quality uniform diamond films.

In this report we present results of chemical vapor deposition (CVD) method, in which the working gas is the mixture of hydrogen (h) and hydrocarbon (h-c). See the *Table*. The important parameters are: time of deposition (t), the gas and the substrate temperatures, gas flow rate (v_h / v_{h-c}), the total gas pressure (p_{tot}), etc.

Table. Typical CVD process parameters.

No	*t (h)*	v_h *(ml/min)*	v_{h-c} *(ml/min)*	v_h / v_{h-c}	p_{tot} *(mbar)*
1	3.0	1650	2.9	569	40
2	3.5	1980	3.7	539	30
3	4.0	1650	2.2	750	40
4	5.0	1650	2.9	569	40
5	5.0	1650	2.2	750	30
6	5.0	1650	2.2	750	40

Nonuniform distribution of substrate temperatures yields to growth of diamond films in a variety of ways and affects on various types of carbon structures.

Using scanning electron microscopy (SEM) we observed a variety of morphological structures and different nucleation densities in diamond films. Additional information, like crystallite sizes, chemical composition of different carbonaceous compounds (diamond structure, microcrystalline graphite, amorphous carbon, "amorphous" diamond clusters, etc.), defects, were obtained due to the Raman spectroscopy and the electron paramagnetic spectroscopy (EPR). A few correlations were made between the results of these three methods of film characterization.

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PROPERTIES OF DLC LAYERS PREPARED USING PACVD METHOD AT VARIOUS TEMPERATURES

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The influence of deposition temperature (20-500°C) on diamond-like carbon (DLC) layers properties were investigated. The layers were prepared using PACVD (Plasma Assisted Chemical Vapour Deposition) method from methane and argon (mixture in ratio 1:1). We used RF generator (500W, 13.5 MHz) to generate plasma. Except temperature, all other parameters (bias voltage, chamber pressure, atmosphere composition, etc.) were kept at the constant values. The layers were deposited on silicon substrates (orientation <111>) and on Ti alloy (Ti-6Al-4V) using SiO_2 interlayer to increase DLC layer adherence to metallic substrates. The layer thickness ranged between 500–600 nm. We used Raman and IR spectroscopy to analyse layer properties. Refractory index was measured as well. As for mechanical properties, microhardeness, stress and wear resistance were obtained. Our results indicated, that deposition rate decreases with increasing deposition temperature. From Raman spectras was evaluated I_D/I_G ratio, which increases with temperature up to 300°C. Temperature dependence of resistivity and V/A characteristics of layers were obtained from electrical measurements. The layer structure was amorphous in the whole temperature range. The layers were polymeric at ambient temperature; near 300°C their structure was destructed as a result of polymer decomposition.

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TSC, DLTS AND CAPACITANCE CHARACTERIZATION OF DIAMOND LAYERS GROWN BY HOT-FILAMENT CVD

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During the last few years a lot of attention has been devoted to the growth and characterization of diamond layers deposited by HF CVD method. Diamond exhibits outstanding semiconductor properties with a wide band gap which is indispensable for use in electronic devices such as high temperature transistors and blue light-emitting diodes. The impurity centers of wide-band-gap semiconductors play a very important role in the device application, but a precise data of them has not been made. One of the key problems in diamond devices fabrication is the doping of electrically active donors and acceptors into diamond produced by HF CVD. The diamond layers deposited by HF CVD are supposed to contain a large amount of defects at present stage of synthesis what would provide an important obstacle if this material is used for optoelectronic applications. This is still a serious problem for diamond in spit e of definite success in the growth of doped, chemical vapour-deposited films.

In this work the parameters of trapping centers in CVD HF diamond films were studied by deep level transient spectroscopy (DLTS), current - voltage (I-V), capacitance-voltage (C-V), temperature stimulated current (TSC) methods. These measurements were made in the temperature range from 70 K to 400 K. The concentrations, activation energies, capture cross-sections and locations of the trapping centers were determined. The DLTS showed that micro defects of the all samples with CVD diamond films are acting as trapping centers (point defects) and have the continuous energy spectrum with three maxima at different energies. It was found that a s-deposited diamond surfaces were characterized by the high density of the surface point defects-electrical active-trapping centers. After thermal treatment of diamond surface with argon plasma the density of defects substantially decreased. In this case Ar plasma induced new point defects and changed their energy distribution. Deep levels with energies E = 0.34 eV, and E = 0.79 eV were obtained from TSC and DLTS spectra of diamond-Si junction.

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ELECTRICAL AND TEMPERATURE PROPERTIES OF THIN ZnS:Mn FILMS

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The electroluminescent thin film cells based on zinc sulphide doped with manganese were investigated. The cells were prepared by thermal evaporation of ZnS thin film onto a glass substrate in a vacuum. Next, Cu_xS layer was formed by a wet chemical method. In the next step, a layer of ZnS:Mn was evaporated from powder previously activated with manganese at concentration of 3 wt. %. Finally, the aluminium electrodes were evaporated. The cells produced in the above described way exhibit electroluminescence when dc voltage is applied in the reverse polarity (with the positive aluminium electrode). The application of the cells is limited by unresolved degradation phenomena. In order to improve the stability, the knowledge of the electroluminescence mechanism is necessary. In our previous papers we have mainly considered spectral and kinetic properties of the cells. We have found that spectral of the electroluminescence contain some structure. Very interesting phenomenon is observed in the luminescence when the cell is excited by short voltage pulse. In this case the maximum of the electroluminescence appears after the end of the exciting pulse. To explain the phenomenon we proposed model assuming energy transfer between monomolecular centres. The model is in good agreement with the experimental data. In this paper we would like to pay special attention to electrical properties of whole cell as well as ZnS,Mn,Cu thin film – normal metal (PtIr). The current and differential resistance versus dc applied voltage was measured using point contact spectroscopy method. From current-voltage characteristics exhibits that there is more then one mechanism of conductivity in the samples. It is found that three mechanisms (space charge limited current, Poole-Frenkle emission and Schottky emission) should be taken into account. In the current – voltage characteristics and differential resistance vs. voltage the memory effect was observed, especially for positive applied voltage. The effect becomes more distinct with decreasing of the sample temperature.

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DESCRIPTION OF THE ELEKTROLUMINESCENCE OF THIN ZnS:Mn FILMS EXCITED BY RECTANGULAR VOLTAGE PULSES

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We have investigated of time dependence of electroluminescence of thin film cells based on ZnS:Mn. The cells were made by thermal evaporation in a vacuum. In many cases the time dependence of luminescence excited by rectangular pulses is described as

$$I = G\left(1 - e^{-t/\tau}\right),$$

during the exciting pulse and

$$I = I_0 e^{-t/\tau}, \qquad (1)$$

after the end of the pulse, where τ is the lifetime of luminescent centres and G is generation rate. Sometimes, the time dependence of luminescence is not described by the equations. The electroluminescence of our cells excited by short pulses increases in intensity after the end of the excitation pulse before subsequently decaying. Such behaviour has also been seen in ZnS:Mn and other compounds. Another interesting phenomenon is the untypical behaviour of the electroluminescence observed during the exciting pulse. The time dependence is considerably different from that for direct excitation, when the width of the exciting pulse is very short. In order to explain the phenomena we assumed energy transfer between two monomolecular centres. For very short exciting pulse we have obtained the dependence

$$I = \frac{N_{01}}{\tau_2 - \tau_1}\left[e^{-t/\tau_2} - e^{-t/\tau_1}\right], \qquad (2)$$

where N_{01} is the initial number of excited transferring centres and τ_1, τ_2 are the lifetime of the transferring and emitting centres, respectively. Assuming that each part of the exciting pulse T produced the elemental curve (2), we obtained time dependence of luminescence during rectangular exciting pulse

$$I = \frac{G}{\tau_2 - \tau_1}\left[\tau_2\left(1 - e^{-t/\tau_2}\right) - \tau_1\left(1 - e^{-t/\tau_1}\right)\right], \qquad (3)$$

and after the pulse

$$I = \frac{G}{\tau_2 - \tau_1}\left[\tau_2\left(1 - e^{-T/\tau_2}\right) - \tau_1\left(1 - e^{-T/\tau_1}\right)\right]. \qquad (4)$$

Using the equations we obtained good agreement between theoretical curves and experimental points.

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INTEGRATED LIGHT OF ELECTROLUMINESCENCE OF THIN FILM CELLS BASED ON ZnS:Mn

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The investigated light output per pulse measurements have been made for dc electroluminescent thin film structures containing ZnS:Mn layer. Excitation was by rectangular ware voltage pulses with pulse lengths from 10 µs to 500 µs. The emission investigated was from the internal manganese transitions. It has found that kinetic curves are not described using the equations of direct excitation, especially for short exciting pulses. The intergrated light of the electroluminescence as function of drive length was shown. For pulse lengths in the range 190 µs – 500 µs the dependence becomes linear. The behaviour is discussed assuming energy transfer between luminescent centres.

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PbSe THIN FILMS ON Si-SUBSTRATE OBTAINED BY PULSED LASER DEPOSITION METHOD

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Lead selenide with an energy gap of 0. 17eV at 77 K is one of the promising materials for application in mid-infrared optoelectronics. Growth of the PbSe layers on Si substrates is advantageous because silicon substrates are available in large dimensions and are also less expensive than other A_4-B_6 substrates. Laser ablation is one of the promising method for preparation of thin films on different substrates. The velocity distribution of the ablated molecules is an important characteristic for determining the structural quality of thin deposited film. In this investigation we applied time of flight spectrometer for composition characterisation of PbSe layers grown on Si-substrate by pulsed laser deposition (PLD).

In this work the PbSe thin films were grown on Si substrates by the pulsed laser deposition (PLD) method. We have used excimer laser (308nm) to ablation of Pb and Se powders and we used the different Pb/Se ration vapours in beams by applied the different number of pulses on the target . The pulse duration was 20 ns, repetition 10 - 15 Hz and the energy per pulse was 50 mJ. The substrate temperature under crystalization of the PbSe layers was in the range 200-550°C. The films were characterized by X-ray diffraction analysis. We present for the first time influence of film thickness and substrate temperature on lattice constant of PbSe grown by ablation method. We have compared integrated intensities for our films and ASTM data for PbSe. The grain sizes of the PbSe films grown on Si substrates were in the range 320-560Å. The largest grain sizes we have obtained for substrate temperature about 280°C.

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PLE ZnCdHgTe FILMS INVESTIGATION

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CdTe and $Zn_xCd_yHg_{1-x-y}Te$ were grown on glass substrates by PLE technology. Pulse Yag;Nd laser with the following parameters was used: wavelength 1.06 µm, pulse duration was about 150 µs, pulse power 0.6 J, pulse repetition frequency 1÷50 Hz. Deposition was carried out on substrates held at temperatures near 290 K. The thickness of investigated films were in the range of 0.065÷0.70 µm.

In order to provide different composition of the solid solution ZnCdHgTe pellets pressed from the powders of binary compounds CdTe, ZnTe and HgTe were used as the targets. To obtain a regular composition of the grown layers the targets rotated around their symmetry axis with distance between the target and substrate in range of 60÷90 mm; deposition time was from 2 to 6.5 h, the growth chamber pressure was about 10^{-4} Tor.

Electric characteristics of the as-grown samples were examined at the room temperature in the wide range of applied bias. Tunneling current was registered on the samples of CdTe films under applied voltage up to 30 V. All samples of quaternary solid solution ZnCdHgTe were demonstrated an intricate current process, namely, the superposition of tunneling and tunneling-recombination current at applied voltage smaller than 2 V. The investigated samples exhibited barrier-like properties under test signal frequency f=1 kHz at 290 K. The weak photosensitivity was also observed under the samples of solid solutions irradiation by the 100 W power light source.The first results of numerical analysis performed according to the experimental data point out the considerable effect of band-gap fluctuations on electric characteristics of the studied samples. The examinations of the structure and composition of the films are under way. The results will be presented in full version of the conference paper.

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ELECTRICAL PROPERTIES OF HgCdTe/Si FILMS DEPOSITION BY LASER ASSISTED EVAPORATION

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Some experimental results concerning of laser-assisted deposition and evaporation of narrow-gap HgCdTe from solid target are presented.

The deposition set-up consisted of a CW CO_2 laser, a vacuum system, and deposition assembly. The laser beam was focused and modulated with a mechanical chopper and then passes into vacuum chamber and strike the target which is rotated. The laser power densities are 104-105 W cm^{-2} and laser pulse duration is about several milliseconds and period of the exposure was shorter then the period of a shade. The layers were deposited on (001) Si and (111) Si. During the evaporation process, the residual pressure was stabilised at around

$1 \cdot 10^{-5}$ torr. The substrate temperature ranged between $300<T<463$ K and separation distance between the target and substrate was 4-12 cm. The film deposition rate was varied from 1 to 30 nm sec^{-1}. After deposition, the layers were allowed to cool slowly to room temperature at rate of approximately 5°C sec^{-1}.

Under visual inspection, the as-grown films had mirror surface. Morphology of the surface was studied with atom force microscope and scanning tunneling microscope , and structural characteristics were investigation by X-ray diffraction (XRD). XRD analysis showed three peaks in the as-deposited films - (111), (222), and (220). This result indicated that the films were highly oriented with respect to the (111). The degree of orientation an increase with thickness h films and for h>1 μm only (111) orientation of the films growth take place. The morphology of the layers of HgCdTe is strongly dependent on growth rate. Examinations of the AFM and STM shows that film has island structure but films grown at high rate has heterogeneous inclusions when to arise a deep crater on the target. The size of the islands increase with a thick of the films.

The layer composition were controlled by optical absorption spectra and Auger-profiling during layer-by-layer etching with Ar+ plasma and correspond to target compositions.

The HgCdTe/Si layers could be produced of both n-type (T<180°C) and p-type (T>180 °C) conductivity with the free carrier concentration of $n,p = (0.1\text{-}10) \cdot 10^{17}$ cm^{-3}. It was shown that manifestation of splashing effect at laser-assisted evaporation of target depended on condition growth and properties of target but not only laser power density.

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LIQUID PHASE EPITAXY GROWTH ON POROUS SILICON FOR PHOTOVOLTAIC APPLICATIONS

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The aim of this work is to grow a Silicon thin layer by Liquid Phase Epitaxy (LPE) on Porous Silicon. This one acts as sacrificial layer in order to transfer the 50 µm epitaxial layer on foreign substrates like ceramics. Only few results have been already published by this growth method in comparison with the Vapor Phase Epitaxy. Many advantages of LPE have influenced our choice for this technique. The simple use of LPE gives it an important advantage. The LPE growth occurs close to the thermodynamic equilibrium and therefore produces high quality epitaxial layers. By transferring the epitaxial layer on foreign substrate, the silicon wafer is reusable. In this work, we use the following procedure:

- Porous silicon formation by HF anodization,
- Eventual pre-heated treatment in H_2 atmosphere,
- LPE silicon growth.

Scanning Electron Microscopy (SEM) and Raman spectroscopy has been performed on porous silicon in order to analyze the pore size versus heat treatment. Various LPE temperature profiles have been tested and corresponding samples have been observed by SEM. We observe a pyramidal growth at the surface of the porous silicon but the coalescence is difficult to obtain. Although obtaining homogeneous layers is our objective, the pyramidal structure is the first step of the work. Other LPE experiments will be performed in order to support the growth of continuous layers.

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ELECTRICAL AND TRANSPORT PROPERTIES OF MACROPOROUS SILICON STRUCTURES

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The dependencies of electron conductivity, concentration and mobility on pore size and concentration were investigated for macroporous silicon structures. The bolometric characteristics of the macroporous silicon were estimated. The ohmic indium contact to macroporous silicon structures was work up, and the temperature dependencies of conductivity, concentration and mobility of electrons, and spectra of excess noise were measured. The starting material consisted of *n*-type silicon with [100] orientation and 2-5 Ω·cm resistivity. Macropores with diameter D_p = 1 - 15 µm and depths h_p = 50 - 250 µm were formed due to the generation and transfer of nonequilibrium holes to the *n*-Si electrochemically treated surface as a result of optical band-to-band electron-hole generation.

The In/*n*-Si and In/macroporous *n*-Si contacts were formed by thermal evaporation of indium in an atmosphere of hydrogen. The temperature regimes of ohmic contact formation on monocrystalline and on macroporous silicon were comparable with the annealing temperature T = 400°C for thermal diffusion of metal through a SiO_x layer. The contact transient resistance equaled $R_0 \approx$ 4-10 $\Omega \cdot cm^2$.

The electron conductivity, concentration and mobility were measured by the 4-probe method at temperatures 77-300 K. The electron conductivity and concentration in two-layer structures of macroporous silicon, and also in a matrix of macroporous layers have a maximum for a macropore volume of V = 0.3 - 0.4. Thus the electron mobility decreases monotonically. The experimental results were explained by a model based on the existence of electron-enriched regions around pores, with thickness $\Delta D \approx 1$ µm formed after electrochemical and chemical treatment of the macropore walls.

The bolometric charateristics of macroporous silicon were estimated using ohmic structures of the type In/n-Si and In/macroporous n-Si. Temperature dependencies of conductivity, concentration and mobility in macroporous silicon emulate the temperature curves of the corresponding parameters for crystalline silicon. The temperature coefficient of resistance ranges from 0.4 - 1% at room temperature to 1.5 - 4% at 77K. Noise level is $(2\text{-}5)\cdot 10^{-9}$ $VHz^{-1/2}$ for frequencies > 10 Hz, and the detectivity of thermal bolometric elements on the base of macroporous silicon might be equaled $5\cdot 10^{9}$ $cmHz^{1/2}W^{-1}$. So the investigated macroporous silicon structures are promising for multi-element thermal sensor fabrication.

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INFRARED PHOTOLUMINESCENCE OF CZOCHRALSKI GROWN SILICON TREATED AT HIGH TEMPERATURE - HIGH HYDROSTATIC PRESSURE

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It is known that pre-annealing of Czochralski grown silicon (Cz-Si) at atmospheric pressure facilitates creation of nucleating centres for oxygen precipitation during subsequent high temperature-high hydrostatic pressure (HT-HP) treatment. The aim of the present work is to study the transformation of oxygen-related defects in Cz-Si subjected to the HT-HP treatment. The investigated as-grown Cz-Si contained high concentration of interstitial oxygen (10-11)x10^{17} cm^{-3}; it represented in fact a metastable oversaturated solid solution of oxygen in silicon. The studied Cz-Si samples were pre-annealed at atmospheric pressure at T=725°C for 20 h. Afterwards the samples were HT-HP treated under argon hydrostatic pressure equal to 1 bar, 100 bar or 10 kbar while annealing temperature varied from 900 to 1350°C. Duration of treatment changed from 5 min. to 5 h. Defects in the HT-HP treated Cz-Si samples were studied by photoluminescence (PL) spectroscopy. PL was excited by the semiconductor laser (λ = 0.66 μm) and recorded at T= 2 K. PL bands with maximum at 807 meV, 845 meV and 889 meV were detected in the PL spectra of the samples annealed at T=900 at atmospheric pressure. The band 807 meV (D1) is related to presence of dislocations and its intensity was distinctly higher than that of other lines, which, presumably, are due to another types of defects (stacking fault, oxygen clusters etc.). Increase of pressure resulted in quenching of the 845 meV and 889 meV lines, whereas an additional dislocations-related line with maximum at 873 meV (D2) appeared. Intensity of the D2 line was several times lower, than the intensity of the D1 line. In the PL spectra of samples annealed at 1027 or 1127°C only the D1 and D2 PL lines were observed. Relative intensity of these two lines varied with pressure and time of treatment, whereas its absolute intensity was lower than the intensity of the same lines in the spectra of the samples annealed at T=900 or 957°C. Increase of annealing temperatures up to 1306 and 1350°C resulted in further decrease of intensities of the D1 and D2 lines. This effect was more evident for the samples treated at comparatively low pressure. The experimental data can be explained in the following way: at T=900-957°C the massive precipitation of oxygen occurred resulting in an increase of the density of dislocations. Increased HP during the HT – HP treatment promoted that effect. An increase of annealing temperature resulted in decrease of the concentration of dislocations but in increase of the concentration of point defects acting as the centres of nonradiative recombination. Enhanced HP during the treatment at > 1127°C prevents creation of dislocations also because of decreased dimension of oxygen precipitates created at such conditions, too small to act as the nucleation centers for creation of dislocations.

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DEFECTS IN LOW OXYGEN CONTENT $SiO_{1-x}N_x$ FILMS SYNTHESIZED BY PECVD

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Silicon oxynitrides ($SiO_{1-x}N_x$) are currently attracting widespread interest because of a variety of possible applications in microelectronic technology. The oxynitrides are more chemically stable than SiO_2, and can retard rapidly diffusing impurities. The Si-$SiO_{1-x}N_x$ interface has a lower density of surface state than the Si-Si_3N_4 interface. Stable and nonporous passivating and masking layers can be prepared on the basis of $SiO_{1-x}N_x$. The defects of the $SiO_{1-x}N_x$ films synthesized by PECVD, at the $SiO_{1-x}N_x$/Cz-Si interface as well as the effect of further film treatment at high temperatures – pressures (HT-HP) on the properties of these defects have been investigated in the present work. The 150 nm thick SiO1-xNx films with a low oxygen content were grown on Czochralski silicon (Cz-Si) substrates. The nitrogen content (x) in the $SiO_{1-x}N_x$ films was above 0.6. In order to densify the films and to the decrease the concentration of growth defects, the films were pre-annealed in an oxygen atmosphere at T_a=1000°C for 30 minutes. Afterwards the films were HT-HP treated under a hydrostatic pressure (HP) of 1 bar, 10 кbar, and 11.5 кbar in argon at different temperatures T_a=900–1100°C for 5 hours. The defects in the films were detected using room temperature photoluminescence (PL) excited by an N_2-laser, λ=337 nm. Two overlapping bands with the maxima at $\hbar\omega$=1.9 eV and 2.2 eV were observed in the PL spectra of the densified films. The positions of these bands and the values of their widths at half-maximum, equal to 0.48 eV and 0.67 eV for the first and second band, respectively, evidence that the bands are originating from the presence the ≡SiO° (≡Si_2N°) and ≡Si-Si≡ defects. This is also confirmed by the values of *1/e* decay times for these bands (23 and 43 μs, respectively). Contrary [1,2], the decay curves were essentially non-exponential, and could be approximated by a power-law dependence $I_{PL}(t) \sim 1/t$. The maximum intensity of the PL bands was observed in the film with the lowest oxygen concentration. A change of the oxygen concentration (1-x) resulted only in a variation in the PL band intensity. Also the treatment both at atmospheric and at high pressures, changed only the intensity of the bands. This means that these treatments do not result in formation of new types of defects in the films, and influence only the concentration of defects. It was found that dependence of the PL intensity on the treatment temperature and pressure was different for the films with various oxygen contents.

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INFRARED STUDIES OF SILICON OXIDE FORMATION IN OXYGEN-IMPLANTED SILICON WAFERS ANNEALED UNDER ENHANCED PRESSURE

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Evolution of silicon-oxide formation in oxygen implanted silicon wafers during annealing under enhanced ambient pressure was studied in present paper.

Oxygen implantation into silicon wafers makes possible to prepare a thin silicon layer well isolated from the rest of the wafer by buried oxide layer – a structure (SIMOX) suitable for very large scale integrated (VLSI) applications. To prepare such structure of high quality the control of oxygen precipitation, coalescence process and defect formation at the Si/SiO_{2-x} interface during the annealing is necessary. Fourier-Transform Infrared Absorption Spectroscopy (FTIR), by controlling the vibrational modes of Si-O-Si bonds, allows for monitoring the process of buried oxide (BOX) formation during implantation and annealing. The process of BOX formation is accompanied by generation of secondary defects at the Si/SiO_2 interface. A number of defects are the centres of radiative recombination and can be detected by photoluminescence (PL) measurements.

Evolution of silicon-oxide formation in oxygen implanted silicon wafers during annealing under enhanced ambient pressure was studied in present paper. Silicon Floating Zone (FZ) and Czochralski (CZ) wafers were implanted with oxygen (doses up to $6*10^{17}/cm^2$) and annealed at 450^0C – 1280^oC (HT) for up to 10h under argon pressure (HP) up to 1.5GPa (HP-HT treatment). HP-HT treated structures were studied by FTIR and PL measurements.

It has been stated that:

- the position of Si-O-Si asymmetric stretching mode is shifted from $1007cm^{-1}$ for as- implanted samples to 1080 cm^{-1} for HP-HT treated, in dependence on the HP-HT conditions,
- enhanced HP influences the creation of dislocation structure significantly. The intensity of D1 and D2 PL lines related to presence of dislocations is strongly dependent on HP, typically decreasing with HP for the samples treated at $T>1000^oC$,
- the composition of SiO_{2-x} is mainly governed by implanted oxygen dose and temperature of annealing,
- enhanced stress at annealing affects oxygen distribution and creation of other (point-like?) defects.

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VERTICAL ELECTRICAL BEHAVIOUR OF Al/SiGe/Si STRUCTURES

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The vertical electrical behaviour of amorphous, polycyrystalline and single-crystalline SiGe layers and Si/Ge, Si/SiGe superlattices prepared on n and p-type Si substrates have been studied. The single-crystalline layers and superlattices were grown by MBE, the amorphous layers and superlattices were prepared by sputtering. The polycrystalline layers were obtained from the sputtered amorphous layers by annealing. For electrical measurements Al Schottky contacts were evaporated on the front side of the wafers. The ohmic contacts were also prepared by Al evaporation on the back side of the wafers. The electrical behaviour were studied by current-voltage (I-V) and capacitance-voltage (C-V) measurements in the temperature range of 80-360 K.

The electrical behaviour strongly depended on the preparation concitions of the studied layers and on their composition and combination. However, most of the structures exhibited similar specific features. The common feature of the I-V characteristics was that they consisted of different parts with different slopes dorresponding to different current mechanisms. For the sputtered layers and superlattices, the first part at low biases showed ohmic behaviour. It was connected with a parallel conductance through some defects in the sputtered layers The most abrupt part at relatively low biases was attributed to a Schottky barrier formed by Al on the sputtered and MBE grown SiGe layers and superlattices. For superlattices, a less abrupt part exhibiting also a linear logI-V relationship was also obtained at relatively high biases. In this part, the current was limited by the conductance through the superlattice. In the last part at high biases, the current was limited by the series resistance. C-V characteristics also exhibited specific behaviour connected with the charge transfer from and to the potential wells formed by SiGe layers or superlattices.

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ANALYSIS OF THE GaAs-Si INTERACTIONS ON THE INTERFACE ENERGY

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GaAs – based semiconductors on Si substrates have attracted much interest as promising materials for future optoelectronic integrated circuits. Liquid Phase Epitaxy (LPE), especially from the economic point of view, is an interesting method for the growth of GaAs on Si substrate. The direct planar LPE growth of GaAs on Si is hardly possible because of the large lattice mismatch (4 %) and the significant difference in sizes of the atoms of two phases.

In previous paper [1] the authors presented theoretical analysis of the interface energy in GaAs/Si heterostructure as a function of crystallographic orientation of the substrate. An algorithm of numerical calculations is based on semiempirical model of covalent bonding in Si, which has four parameters [2]. In order to find values of these parameters for GaAs we have performed analysis of the influence of their values on the interface energy. Since the interface energy depends on the surface energy of two phases [3] we have carried out calculations for homostructure GaAs/GaAs with different planes of GaAs for which the surface energies are known. We have found the values of four parameters for GaAs and we have used them for further analysis of the interfacial energy of GaAs/Si heterostructure as a function of substrate misorientation.

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COMPARISON OF CSVT, LPE, AND VPE GaAs AND AlGaas LAYERS BY ELECTRICAL MEASUREMENTS

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The electrical behaviour of n-type GaAs and AlGaAs epitaxial layers grown by different ways and with different composition, respectively, have been studied by using Shottky junctions as test structures. The GaAs layers were grown by close spaced vapour transport epitaxy (CSVT), by liquid phase epitaxy (LPE), and by vapour phase epitaxy (VPE) based on chloride transport. To study the effect of the water vapours on the epitaxy, VPE layers with the presence of water vapours in the reactor chamber were also grown. The AlGaAs layers were grown by LPE in the range of AlAs content of 0-0.3. For electrical measurements, Al Schottky contacts were evaporated on the front side of each types of wafers. As the preliminary results obtained on these structures indicated the interaction of Al with GaAs and AlGaAs, Au, Ge, Ni and Ti Schottky junctions were also prepared on the ordinary VPE layers. The ohmic contacts were formed by AuGe euthectic on the back side of the wafers. The electrical properties were studied by current-voltage and capacitance-voltage measurements in the temperature range of 80-360 K.

The electrical behaviour of Al/GaAs junctions strongly depended on the method of epitaxy. The Schottky barrier height varied between 0.72 eV (obtained for the water-assisted VPE layers) and 0.88 eV (obtained for the ordinary VPE layers without water vapours). The lowest ideality factor of 1.14 was obtained for the LPE layer, while for the ordinary VPE layers its value was 1.25. However, Au/GaAs junctions prepared on ordinary VPE layers exhibited a much lower ideality factor of 1.05. This indicates that Al interacted really with GaAs, as it was indicated by preliminary results. The actual mechanism must be the diffusion of Al into GaAs during processing. This mechanism was confirmed by the results of heat treatment experiments performed on these junctions. Annealing (up to 350 ^{o}C) enhanced the Schottky barrier height.

The behaviour of junctions prepared on AlGaAs layers depended on the AlAs content. The obtained barrier height values were in agreement with our prediction concerning the Fermi-level pinning position at the metal/AlGaAs interface. Due to this prediction the Fermi-level is pinned at 1.15±0.10 eV below the L-band minimum. The obtained barrier height data are within this range.

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C-V PROFILING OF GAAS USING ELECTROLYTE BARRIERS

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Modern epitaxial growth techniques can provide abrupt multidecade doping transitions over a spatial range of a few angstroms. Doping layers with precise profiles and impurity concentrations are the most important properties of semiconductor epitaxial layers used for the fabrication of devices. Therefore, the ability to accurately characterise these doping transitions is of considerable value.

Usually, doping concentrations are determined from homogenously doped calibration layers and are frequently measured by the method using a metal Schottky contact. As it is well known, the standard method requires a variable dc bias applied to the Schottky contact for varying the depletion depth at which the impurity concentration is measured. A range of the depth in which measurements can be carried out is restricted due to avalanche breakdown. This is the reason that for calibration measurements a few bulk layers grown in independent processes doped with impurities in a wide range of concentration are required. This is why the doping calibration based on the conventional C-V measurements is time consuming and expensive.

In order to overcome the principal limitation of the method it was common practice alternately to etch the sample chemically (to remove controlled amounts of materials) and make profile plots using an electrolyte to make the Schottky contacts. The advantage of the electrochemical C-V depth profile is the possibility to study a few layers with different doping levels grown on the same n^+ - substrate in one growth run. The disadvantages of the method are that it is difficult to measure and control the area of the electrolyte contact with high precision and the depth resolution is limited by etching non-uniformity. In this note, we use the method of the electrochemical profiling to characterise n-type GaAs grown by molecular beam epitaxy (MBE). We show that the latter is a serious problem, even in the case of a good quality material and suppose that the effect is caused by the presence of the surface oval defects which are typical defects for the epitaxial growth.

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MOVPE GAN GROWN ON ALTERNATING SUBSTRATES

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Gallium nitride and their related alloys InGaN and AlGaN are important materials for short wavelength optical devices and high power, high frequency devices due to their wide band gap and good thermal, chemical and mechanical stability. The lack of the lattice-matched substrates makes the GaN devices difficult for commercialisation. Devices heterostuctures are typically grown by metalorganic vapour phase epitaxy (MOVPE) or molecular beam epitaxy MBE on sapphire or SiC using low temperature buffer layers. Due to the lattice mismatch between the substrates and nitrides the large numbers of dislocations are generated. New, alternating, substrates such as ZnO, NdGaO, YSZ have much better lattice matching (when cutting them along relevant planes) and/or closer thermal expansion coefficients, so they are promising for the epitaxial growth of nitrides. We investigated the structure, morphology and optical properties of GaN films deposited on alternating substrates by MOVPE technique. Scanning electron microscopy, X-ray diffraction, photoluminescence and impedance spectroscopy analyses were used for the epitaxial layers characterisation. The obtained results have been compared to those of GaN layers grown on c-plane sapphire substrates.

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LPE GROWTH AND CHARACTERIZATION OF $In_xGa_{1-x}As_ySb_{1-y}$ QUATERNARY ALLOYS ON GaSb

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The quaternary alloy $In_xGa_{1-x}As_ySb_{1-y}$ lattice matched to GaSb substrate is a material of great interest for optoelectronic devices operating in the mid infrared wavelength region (from 1.7 to 4.4 μm). The potential applications in this wavelength domain are gas spectroscopy analysis, optical transmission through the atmosphere, and light-wave communication systems to mention but a few.

Nearly lattice matched ($\Delta a/a < 1.5x10^{-3}$) $In_xGa_{1-x}As_ySb_{1-y}$ layers with $0 < x < 0.20$ were grown by liquid phase epitaxy (LPE) on (100) oriented GaSb. The LPE growth was carried out in a quartz reactor tube heated by a single-zone semi-transparent furnace. The layers were grown from single-phase solutions prepared from pure (6N) In, Ga, Sb and from undoped ($n \approx 10^{15}$ cm^{-3}) GaAs. The melts were homogenized and purified 2 hours at 670 ^oC. Then the temperature was quickly reduced to 530 ^oC. During further reduction of the temperature from 530 ^oC to 520 ^oC the cooling rate was kept constant. The layer thickness was about 4 to 6 μm.

The grown $In_xGa_{1-x}As_ySb_{1-y}$ layers were characterized by X-ray diffraction (XRD) and X-ray microprobe (XMA) measurements, and the band gaps were determined from the analysis of the variation of the optical absorption coefficient with the photon energy determined from room temperature optical transmission measurements. The dependence of the band gap on the composition exhibits smaller bowing than given by recent theoretical calculations based on the correlated function expansion technique. Near and below the fundamental absorption edge an exponential absorption tail corresponding to the Urbach rule was observed which is ascribed to the effects of the random potential due to the alloy disorder.

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EPITAXIAL GROWTH AND CHARACTERISATION OF SILICON δ-DOPED GaAs, AlAs AND $Al_xGa_{1-x}As$

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Recently, the δ-doping has become the most important doping method for advanced semiconductor structures. This technique, which spatially confines dopant atoms within one atomic layer, has been extensively studied due to its attractive features for both fundamental interests and novel device applications such as: HEMT, resonant tunnelling diodes (RTDs), quantum well infrared photodetectors (QWIPs). This work presents investigation of MOVPE growth of silicon δ-doped GaAs, AlAs and $Al_xGa_{1-x}As$ epilayers and different methods used for their characterisation. All investigated epitaxial structures were grown on semi-insulating GaAs substrate using an atmospheric pressure horizontal AIX 200 Aixtron reactor. Delta doping was formed by introduction of SiH_4 during the growth interruption. The influence of the growth temperature and $Al_xGa_{1-x}As$ composition on delta-doping characteristics, carrier concentration and mobility is discussed. Properties of the investigated Si δ-doped structures were examined using capacitance-voltage (C-V and EC-V) measurements, Van der Pauw-Hall measurements (300K, 77K), photocurrent (PCIV) measurements, photoreflectance (PR) spectroscopy and X-ray (HRXRD) measurements. Best results of δ-doping process were obtained for Si δ-doped GaAs grown at 670°C. For this layer the narrowest C-V profile with the $FWHM_{C-V} \approx 5nm$ and the electron peak concentration of $5.2\times10^{18}cm^{-3}$ were obtained. This sample exhibits also the best PR spectrum with above 20 extremes distinguishing Franz-Keldysh oscillations. Based on PR spectra obtained for different kinds of Si δ-doped structures, the built-in electric field and the value of the potential barrier height between the surface and the δ-doped region were calculated. The Van der Pauw-Hall measurements made at 300K and 77K for δ-doped $Al_xGa_{1-x}As$ (x=0.29, 0.34, 0.46, 0.6) showed that for high sheet carrier concentrations ($N_s > 10^{13}cm^{-2}$) the mobility is independent on temperature. In the case of lower carrier concentrations ($N_s = 10^{11} \div 1.2\times10^{12}cm^{-2}$) the mobility is temperature dependent and shows considerable increase at low temperatures. Additionally, the mobility decreases with increasing $Al_xGa_{1-x}As$ composition. Photocurrent measurements of δ-doped $Al_xGa_{1-x}As$ eplayers showed the generation of carriers in $Al_xGa_{1-x}As$ and GaAs interface layer in the case of high sheet concentration. For the samples with lower sheet concentration the GaAs/$Al_xGa_{1-x}As$ interface plays a dominant role due to the formation of 2DEG, what is shown as the long wavelength tails of the obtained spectra. The presented investigations are essential for elaborating the technology of high quality δ-doped $Al_xGa_{1-x}As$/GaAs structures for advanced device applications.

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X-RAY DIFFRACTOMETRIC MEASUREMENTS OF THE (Al, Ga)N EPITAXIAL LAYERS

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(Al,Ga)N structures belong to the most popular wide - bandgap semiconductors. Methodology of the structural characterization by means of X-ray diffractometry is presented. In order to obtain the necessary information the high resolution as well as parallel beam optics were supplied. The examined layers were .deposited in MOVPE system on c-plane sapphire substrate. The following parameters were determined: distribution of the AlGaN lateral and vertical lengths, strains, twist and tilt mosaicity.

The grains sizes were calculated on the basis of the peak profiles analysis and solution of the Fredholm equations [1] [2]. Twist and tilt mosaicities were measured directly from the specially chosen rocking curves - (110) and (020). In order to obtain such reflections the new geometry of the scans was proposed, were the edge (not surface) of the sample was illuminated [3]. Additionally the data obtained for the typically measured rocking curves and reciprocal lattice points (RLP) were presented – (002) (004) (006) (114) (-1-14) and discussed.

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EFFECT OF HIGH TEMPERATURE – PRESSURE ON AlGaAs LAYERS GROWN ON GaAs AND Si SUBSTRATES

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Due to different compressibility and thermal expansion of the substrate and layer materials, annealing of heterostructures at enhanced hydrostatic pressure of ambient (HT – HP treatment) can affect the strain state of the layers. In effect of the HT – HP treatment, additional defects related to initially present structural irregularities can be also generated.

Effects of the miscut angles of the substrates and of the temperature and pressure during the HT – HP treatment on the crystallographic properties of originally strained AlGaAs / GaAs and of partially relaxed GaAs / Si heterostructures are investigated in this work. The 1.5 μm and 2 μm thick AlGaAs layers were grown on the (001) oriented GaAs and Si substrates by molecular beam epitaxy (MBE). The miscut angles of the substrates were in the 0 - 4.5^o range. The investigated samples were HT - HP treated at 670 - 1070 K under 0.6 -1.2 GPa argon pressure for 1 h in a specially designed high pressure furnace.

X-ray investigations were carried out using high - resolution MRD Philips diffractometer in the double - crystal and triple - axis configurations. The structural changes of the AlGaAs layers determined by X – ray methods were compared with that detected by photoluminescence measurements.

The structural properties of epitaxial AlGaAs semiconductor layers subjected to the HT – HP treatment depend strongly on their initial strain state, defect structure, treatment pressure and temperature, while do not exhibit any measurable structural changes after annealing at 670 K - 10^5 Pa. For the GaAs / Si structures, the residual strain in GaAs layers decreased after the treatment; the GaAs / Si sample bending decreased also. The observed HT – HP induced effects in the GaAs / Si samples can be explained taking into account strain relaxation at high pressures – temperatures. For the AlGaAs / GaAs samples, the similar relaxation effect was observed only at the highest pressures and temperatures, mostly due to very close bulk modulus values of the substrate and layer materials. At lower HT - HP the changes of structural properties depend mainly on the initial layer defect structure.

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STRUCTURE CHARACTERISATION OF ALN LAYERS OBTAINED WITH REACTIVE SPUTTERING METHOD

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One of the most important parameter of semiconductor lasers it their lifetime, which to a large expend depends on the quality of reflecting, layers - mirrors. Currently a number of research has been carried out to develop mirrors resistant to heat produced by radiation absorption. One of the methods to solve this problem is the application of AIN layers. The presently studied AIN layers have been obtained by means of AIN target sputtering in reactive Ar + N plasma. AIN layers of thickness from 2 to 5 μm have been deposited on Si substrate. Multiple AIN-Si layers of thickness 1000Å each where also studied.

Description of samples' quality has been obtained using various analytical methods. An initial selection of samples with appropriate refraction coefficient ($n = 2 \pm 0,2$) has been made by ellipsometery. Thickness of samples was measured by ellipsometer and profilemeter (α-step). Morphology of the surface has been examined with Scanning Electron Microscope (SEM), while the structural analysis has been performed using Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) techniques. The multi-layer structure was additionally tested the RBS (Rutherford Backscattering Spectrometry).

The X-ray diffraction measurements performed with grazing incidence technique confirmed that the investigated samples were of hexagonal structure with lattice parameters slightly increased with respect to the database values. The preferential lattice orientation of (002) planes was found. The diffraction patterns proved the existence of well-developed crystallites. The size of crystallites increased with increasing layers thickness. In all cases the morphology of the AlN-layers is characterised by columnar structures. According to SEM, the surface roughness is limited by size of crystal grains. RBS experiments proved that multi-layer structure consists of two Si layers with thickness of 46,1 nm and 41,0 nm and two AlN layers with thickness 79,9 nm and 79,3 nm. In the TEM high-resolution picture single crystalline grains were observed.

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X-RAY DIFFRACTION STUDIES OF COMPOSITION INHOMOGENEITIES IN $Ga_{1-x}In_xN$ THIN LAYERS

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In this study we investigate inhomogeneities due to alloy fluctuations in MOCVD grown $Ga_{1-x}In_xN$ thin films (25 nm ≤ t ≤ 75 nm) in the compositional range $0 < x \leq 0.093$ deposited on 3 µm GaN sublayers grown on *c* sapphire plane. InGaN films are analyzed by high resolution x-ray diffraction. X-ray diffraction profiles and reciprocal space maps are measured in the triple-axis mode. The previously observed anisotropy of strains is taken into account in the experiment and all x-ray measurements were carried out for one scattering vector $\boldsymbol{q}_x$. Films grown with the lower In content ($x \leq 0.085$) revealed compositional inhomogeneity as a single extra peak in the diffraction rocking curve which can be attributed to local bilayer growth of the ternary. Films grown with the higher In content exhibited both an smearing of diffraction profiles (quasi-continuous compositional changes) and development of multiple peaking that correspond to local-domain growth. Non-uniform epitaxial growth results in a composition distribution of the ternary, derived by x-ray measurements, which is compatible with the value of composition obtained from RBS characterization [1].

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BASIC PROPERTIES OF POLYCRYSTALLINE InSbBi AND InSbAsBi THIN FILMS PREPARED BY THE FLASH-EVAPORATION METHOD

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The most frequently used in optoelectronics material in the IR window 8-12 µm is CdHgTe. However, this mixed crystal material shows an important failure that its material parameters, change with time. Hence, the problem of finding a new stable material for this optical range is still topical. Till now, most effort was concentrated on the obtaining mixed crystals with the desired band gap based on InSb. Here, the known property of the III-V compounds that the band gap decreases with the mass of the component atoms is exploited. The only exception from this rule is the substitutions of Sb atoms with As atoms in the $InSb_{1-x}As_x$ mixed crystal with $x < 0.4$.

In this contribution we report on preliminary studies of $InSb_{1-x}Bi_x$ and $InSb_{1-2x}As_xBi_x$ thin films obtained for the first time by the flash-evaporation method using the mixture of powders of high purity crystals of InSb, InBi and InAs. Most of the reported properties of $InSb_{1-x}Bi_x$ thin films dealt with the films obtained by the MBE and the MOCVD methods. In those films (as well as in bulk crystals) the maximum Bi content obtained was usually smaller than 3%.

A great advantage of the flash-evaporation method is an easy control of the chemical composition of the vapour stream and performing the film deposition on the (desirable) In-rich side of the process. An important point of our investigations is checking if the gap narrowing observed in $InSb_{1-x}Bi_x$ and $InSb_{1-x}As_x$ is of a cumulative type in the case of $InSb_{1-2x}As_xBi_x$ ($x \leq 0.2$). The films investigated here were about 2 µm in thickness and were deposited in high vacuum on ceramic substrates kept at temperature of 380°C.

The film morphology and chemical composition were investigated by a scanning electron microscope and X-ray microanalyser. These investigations revealed a number of inclusions on the film surface for $x>0.05$. The inclusions were composed mainly of Bi and their density increased with x. The content of Bi in the film matrix, independent of the value of x in the starting material (i.e., in the vapour phase), never exceeded about 3.5 atomic %. On the other hand the values of x for As in the starting material and the films were about the same. Additional X-ray studies confirmed the polycrystalline character of the films and appearance of the Bi phase. In the $InSb_{1-2x}As_xBi_x$ films the lattice parameter changes were in accord with the As content. In the case of $InSb_{1-x}Bi_x$ films no measurable change in the lattice parameter was found. This may mean that the Bi atoms were mainly incorporated into the lattice as interstitials.

The expected changes in the energy gap width were investigated by the temperature dependence of the Hall coefficient and optical absorption measurements. Whereas, the electrical measurements suggest a considerable decrease in the gap in the $InSb_{1-2x}As_xBi_x$ films, the optical data seem do not confirm t. Possible reasons of the lack of consistency in the experimental results are discussed.

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A SIMPLE ALGORITHM FOR THE RECONSTRUCTION OF SURFACE TOPOGRAPHY FROM MAKYOH-TOPOGRAPHY IMAGES

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Makyoh topography that is based on the principle of the ancient Japanese magic mirror, has proved to be a powerful topographic tool for the qualitative visualisation of the surface morphology of mirror-like surfaces. Its principle is the following: The sample is illuminated by a collimated light beam, and the reflected image is visualised in a screen placed some distance away from the sample. The irregularities of the sample surface disturb the reflected light beam, thus the reflected image will reproduce the sample morphology. This technique is applied mainly for the assessment of the polishing quality and large-scale deformation of semiconductor wafers and other crystal surfaces. Makyoh-topography instruments are available commercially as well. Makyoh gained its success due to its simplicity, high dynamic range, low cost and real-time operation. However, the interpretation of Makyoh images is not straightforward. Recently, ray-tracing simulations were made for some specific cases and the image formation was interpreted within a geometrical optical framework. The ultimate aim is the reconstruction of the surface morphology from the observed Makyoh image. This contribution presents an iterative algorithm for this task, based on geometrical optics. The geometrical optical approximation is justified, since the studied samples usually possess more or less uniform reflectivity; diffraction effects appear only at the sample edges and around non-reflecting surface defects. The algorithm is tested on simulated one-dimensional surfaces; the working limits, errors, and the effect of imaging and model parameters are analysed in detail.

Acknowledgements

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SIMULATION OF ION-ASSISTED DEPOSITION PROCESS (IBAD) IN SEARCH OF A HIGH QUALITY OPTICAL FILMS. A MONTE CARLO SIMULATION STUDY

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A Monte Carlo simulation model of the ion-assisted deposition process (IBAD) has been used in order to investigate the influence of some process parameters on the final morphology and quality of the thin films. The simulations were performed on a simple cubic lattice with the Metropolis sampling algorithm employed. The mechanism of internal rearrangements of deposited adatoms has been introduced into the model. The results show that the angle of ion beam as well as the kinetic energy particles, ion-to-atom arrival ratio (IAR) and the roughness of the substrate play an important role in the morphology of obtained films. Also the influence of the parameters on morphology of the films has been discussed.

The detailed description of the Monte Carlo model of the IBAD growth process has been presented in our previous paper . The model uses a simple cubic lattice what makes the idea simple and speeds up the calculations. On the other hand the lattice approximation is reasonable in the solid state thin films. The adatoms as well as arriving ions can be located in lattice points only. The beam of atoms (originating from the Kaufman source) of deposited material is perpendicular to the layer of substrate on which the deposition takes place. The process of the deposition of material atoms is accompanied by a beam of ions, which arrive at certain angle with respect to the normal . During the deposition process the interaction between the growing film (consisting of adatoms and ions) and the arriving particles (atoms and ions) takes place. The results show also that the model taking the pinning effect under consideration enables one to obtain more dense layers.

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FORMATION AND GROWTH OF LENNARD-JONES CLUSTERS – MONTE CARLO SIMULATION

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Formation of Lennard-Jones clusters containing 201 atoms have been simulated [1] using canonical Monte Carlo method at the reduced temperatures between T=0.05 and T=0.49. It has been shown that starting configurations with initial placement of atoms near the centre of a simulation box and allowed movement of entire clusters lead to faster attaining of equilibrium in the system. Local arrangement of atoms within clusters has been identified using a specially invented algorithm based on automatic classification of four types (hcp, pdp, fcc and ic) of regular coordination polyhedra, each having 12 first neighbours in the corners. In solid clusters (T<0.38) the sequence of local structures abundance is the following: hcp, pdp, fcc and finely ic. In liquid clusters only short living ic structures were detected. Then, simulation of cluster growth started from selected 201 atom cluster as a nucleus, which grow until large nucleus/cluster, composed of ca. 4000 atoms, was obtained. Addition of single atoms as well as small clusters, if formed as a result of random atom collisions, was enabled during nucleus growth. Changes in internal structure of growing nucleus were monitored in order to observe transition from hcp (dominating in medium sized LJ clusters) to fcc structure (typical for bulk LJ crystals). Moreover, changes in local structure and nucleus shape were analysed as a function of vapour density/supersaturation around growing nucleus. Finally, a selected cluster having pentagonal symmetry axis was used in attempts to grow multiply twinned particle of uniaxial pentagonal symmetry.

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DEFORMED CUBIC fcc (111) OVERLAYER STRAIN ENERGY DENSITY IN ANISOTROPIC APPROACH

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In the elastic continuum approach, the condition for an overlayer to have a free surface normal to the local $\bar{z}$ -axis is that stress components acting on the free surface vanish. If the interfacial interaction has no z-components the strains and displacements will be restricted to the XY-plane, i.e. plane strain. Under these conditions the strain energy density and the stress-strain matrix in the local system become

$$W = \frac{1}{2}\Omega\left[\bar{D}_{11}\bar{\varepsilon}_x^2 + \bar{D}_{22}\bar{\varepsilon}_y^2 + 2\bar{D}_{12}\bar{\varepsilon}_x\bar{\varepsilon}_y + \bar{D}_{33}\bar{\varepsilon}_x\bar{\varepsilon}_y\right] \tag{1}$$

with

	$\bar{\varepsilon}_x^2$	$\bar{\varepsilon}_y^2$	$\bar{\varepsilon}_x\bar{\varepsilon}_y$
$\bar{\sigma}_{xx}$	$\bar{D}_{11}$	$\bar{D}_{12}$	0
$\bar{\sigma}_{yy}$	$\bar{D}_{21}$	$\bar{D}_{22}$	0
$\bar{\sigma}_{zz}$	0	0	$\bar{D}_{33}$

We have calculated the $\bar{D}_{ij}$ matrix elements for fcc (111) overlayer. The $\bar{D}_{ij}$ may be expressed in terms of transformed stiffness constants, from the principal to the local system (1,2)

$$\bar{C}_{ijkl} = T_{Ii}T_{Jj}T_{Kk}T_{Ll}C_{IJKL} \tag{2}$$

In wiev of the symmetry and the fact that many stiffness constants vanish the transformation calculations simplify greatly, yielding the results in contracted notation. For example, for $\bar{C}_{33}$ we obtain:

$$\bar{C}_{33} = \left[T_{31}^4 + T_{32}^4 + T_{33}^4\right]C_{11} + 2\left[T_{31}^2T_{32}^2 + T_{32}^2T_{33}^2 + T_{33}^2T_{31}^2\right](C_{12} + C_{44}) \tag{3}$$

In addition the set of useful stiffness constant transformations we have also derived an error probes, i.e. equations for checking the correctness of the transformed quantities when reduced to an isotropic medium. Based on our transformations we have computed the transformed stiffness constants, Hookian relations and strain energy density applied for Si (111) free surface in the connection with the thermal stress/strain estimation of silicon-based sensors [1].

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SURFACE STATES SPECTROSCOPY IN MS-STRUCTURES BASED ON Ag_3SbS_3 MATERIAL

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The abstract reports results of numerical simulation performed in order to explain electric characteristics of MS-structures based on Ag_3SbS_3 semiconductor. Presence of charge states localized at the interface Ag_3SbS_3/AgO (native oxide) is taken into account. Electric measurements (current-voltage and capacitance-voltage) demonstrated barrier-like characteristics typical for the double-saturation diode-like structures sufficiently effected by the interface charge states. Studies carried out at the room temperature exhibited space-charge limited (SCL) current observed in velocity saturation mode and ballistic regime. Numerical modeling of the experimental data manifested charge carriers transport limited by the oxide-semiconductor barrier height of which was depended upon surface states filling degree determining in turn by the applied bias.

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CONTROL OF PARAMETERS OF III-V MICROCRYSTALS AND EPITAXIAL LAYERS BY MEANS OF COMPLEX DOPING WITH EXTRA ADMIXTURES

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Influence of complex doping of InSb, InAs microcrystals and GaAs epitaxial layers upon their electrophysical parameters (resistivity, concentration and mobility of free charge carriers), their time stability and resistance to fast neutron irradiation. Sn, Te, Au, Al, Yb, Cr and Mn in various combinations were used as the doping impurities. Microcrystals were grown by the vapor phase method of chemical transport reactions in closed system. I and Br were used as the transporting agent. Epitaxial layers were grown by means of LPE method. Sn and Te were used in technology as main donor impurities in order to provide needed level of free charge carrier concentration in microcrystals and films - $2\cdot10^{16}$ - $7\cdot10^{18}$ cm^{-3} for InSb microcrystals, $5\cdot10^{16}$ - $5\cdot10^{18}$ cm^{-3} for InAs microcrystals and 10^{17} - 10^{18} cm^{-3} for GaAs epitaxial layers. Rest of impurities were used in order to modify growth process and material parameters – stimulation of microcrystal growth, increase of charge carrier mobility заряду, improvement of radiation resistance of crystals and films, enhancement of time stability of materials before and after irradiation. It is determined that Au impurity is necessary catalyst for growth of InAs whiskers, and it intensifies InSb microcrystal growth. Its doping nature depends upon availability of other impurities, in particular Sn impurity. Isovalent impurity Al allows to increase electron mobility in InSb microcrystals within some concentration intervals. Cr impurity promotes improvement of radiation resistance of microcrystals. For GaAs epitaxial layers increase of free charge carrier mobility is reached by means of doping with rare-earth elements (in particular Yb) during its growth. Increase of its concentration in initial gallium melt leads to decrease of electron concentration in growing layers, which may cause the conduction type inversion from electron to hole one. P-type is observed at Yb concentration of about 0.008 mass % in the melt. Possibility is shown of efficient application of obtained materials for development of Hall sensors which would operate efficiently under extreme environmental conditions, in particular under hard radiation conditions.

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INVESTIGATION OF GaAs AND GaPAs WHISKER GROWTH

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Semiconductor whiskers are grown by well known chemical vapour deposition (CVD) method which is widely used [1]. Present work deals with an investigation of growth and doping peculiarities of GaAs and GaPAs whiskers obtained in closed halogenide system.

GaPAs (GaAs) whiskers are grown from GaP and GaAs source materials by use of such impurities as Cu, Zn, Te, S, Ni, Au as initiators of growth by vapour-liquid-crystal (VLC) mechanism. GaPAs whiskers under investigation have different contents of As (up to 50 w.%). In one tube the whiskers of various diameters ranging from 0.5 to 200 µm are obtained. All the whiskers grow in <111> direction while their morphology essentially depends on doping impurities. For example in the case of GaPAs whisker growth, the use of Cu leads to creation of triangular prisms while at high doping level of Te and S the ribbon and plate-like crystals are formed. The crystal growth kinetics was also investigated. The growth velocity was determined as ratio of whisker length to growth time. The kinetic coefficient estimated for $GaP_{0.4}As_{0.6}$<Cu> whiskers is equal to 10^{-2}cm/s. Doping of GaAs whiskers by various impurities is found to change the kinetic growth coefficient up to 1 cm/s. From the dependencies of kinetic growth coefficient on temperature the whisker crystallization energy was calculated. The obtained values of crystallization energy (123 kJ/mol for GaPAs whisker, and 97 kJ/mol for GaAs whiskers) are the evidence of the whisker growth by VLC mechanism.

An influence of complex doping on the whisker structure and morphology was investigated. A model based on evaluation of impurity activity coefficients in the whiskers was proposed. High impurity activity coefficients were established to correspond to submicron whisker growth. As the impurity activity coefficient decreases, the whisker morphology changes from twinned ribbons to needle-like crystals with perfect surface and structure. A correlation between impurity activity coefficient and the whisker growth kinetics was found. The impurity activity coefficient (k_a) is smaller, the kinetic growth coefficient (b) is lower. For example, use of Zn impurity with k_a = 0.0025 provides growth of GaAs whiskers with b=1.5 cm/s, while doping of Au with k_a =10^{-7} leads to the whisker growth with b=0,36 cm/s.

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MECHANICAL AND PIEZORESISTIVE PROPERTIES 0F CVD-GROWN Si WHISKERS AT HIGH STRAINS

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Silicon whiskers (SW) have unique properties such as high structure perfection, morphology and miniature size. Due to this they are the interesting objects, for investigation of mechanical and piezoresistive properties under high strains. These whiskers are grown by well-known chemical vapor deposition (CVD): chemical transport reactions from the vapor phase in closed Si-Au-Br system.

This method of crystal growth provides SW's with [111] growth direction, SW are formed as hexagonal prisms, 1...100 µm in width and 1...20 mm in length with doping density and electric resistivity varying in the wide ranges. Identification of crystal faces and crystallographic orientation was carried out by known X-ray methods.

Experimental study of morphology and mechanical properties of grown silicon whiskers, showed their high mechanical strength close to theoretical limit, that differs SW's by their properties from bulk crystals obtained by standard technologies. This special property of SW is due to their high structural perfection, that is the main advantage of this microcrystals. The mechanical strength σ_{max} of whiskers depends on their diameter: the less diameter, the higher strength. Si whiskers with 20…40 µm diameter have an ultimate strength in the range 3…2 GPa, whereas thin crystals with diameter d ≤ 10 achieve 4 GPa and higher.

For the first time theoretical and experimental investigations of longitudinal piezoresistance in p-type boron doped Si whiskers with the impurity concentration $1x10^{18}...3x10^{19}$ cm^{-3} were carried out in the wide strain rang ε = -1.2%...+1.0 %. The piezoresistance dependence from strain essentially depends on a sign of strain. The effect of piezoresistance saturation was observed only at high compressive strain.

Developed high sensitive sensors on the basis of Si whiskers with boron concentration $5x10^{18}$ cm^{-3} for enlarged strain measurements (up to ε = ±1 %) are described. One should note the following advantages of these sensors based on Si whiskers:

i. high sensitivity to strain, their gauge factor ≥ 100 at 20°C;
ii. high mechanical strength and possibility to measure high level of elastic strain up to1% without fracture
iii. the wide operating temperature range –110…+160°C.

Developed silicon sensors were successfully used for testing several constructions until their destruction at dynamic conditions.

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DIMENSIONAL QUANTOZATION IN WHISKERS

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In whiskers, having a small radius r and a length $l_z >> r$ one can observe the dimensional quantization of the carrier energy.

It is possible to prove that the carrier wave function $\Psi_{n,m,kz}(\vec{\mathbf{r}})$ and its dispersion law $\varepsilon_{n,m}(k_z)$ in whiskers are described by the following functions

$$\Psi_{n,m,kz}(\vec{\mathbf{r}}) = \frac{J_m\left(\lambda_n^{(m)}\rho / r\right)}{r\pi^{1/2} J_{m\pm1}\left(\lambda_n^{(m)}\right)} U_{kz}(z) \exp[i(m\varphi + k_z z)], \qquad (1)$$

$$\varepsilon_{n,m}(k_z) = \frac{h^2 \lambda_n^{(m)2}}{8\pi^2 m_0 r^2} + \varepsilon(k_z), \qquad (2)$$

In these formulas $J_m(x)$ are the first-sort Bessel functions, $U_{kz}(z)$ is the modulating Bloch's function, $\rho=(x^2+y^2)^{1/2}$ is the radial coordinate of a carrier in the crystal, $\lambda_n^{(m)}$ is the n-th root of the m-order Bessel function. $J_m\left(\lambda_n^{(m)}\right)=0$ for high enough n, m and the root has such an asimptotics: $\lambda_n^{(m)} \approx \left(n^2 + m^2/\pi^2\right)\pi^2$.

Thus, according to (2) the carrier energy in a whisker is a quantizated value:

$$\varepsilon_{n,m}(k_z) = \frac{h^2\left(n^2 + m^2/\pi^2\right)}{8 m_0 r^2} + \varepsilon(k_z), \qquad (3)$$

with m_o as a free-electron mass; n,m as quantum numbers for the dimensional quantization of the carrier energy in the whisker along the radial direction of the movement. $\varepsilon(k_z)$ is an energy law for the carrier movement along the whisker's longitudinal axis; it is an even and periodical function of k_z.

The calculations prove that the dimensional quantization effect in whiskers appears in crystals having a thickness r_k corresponding to the condition:

$$r_k \approx h / \sqrt{8 m_0 k T}\ . \qquad (4)$$

If $d >> r_k$, then the dimensional quantization vanishes and the bulk energy law is valid.

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GROWTH OF WHISKERS IN AMORPHOUS FILMS

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The many compounds and the pure chemical elements whiskers are know at present. Some models of the whiskers growth have been suggested. However, the whiskers growth processes still to the last failed to understand.

The main aim of this work is to investigate the processes taking place in Sb and $NaSbS_2$ amorphous films after their condensation and subsequent long-term storage at normal conditions.

Samples for the investigation were prepared by vacuum technology: flash evaporation or pulse laser evaporation (PLE) and by deposition onto cleavages of alkali halide single crystals or glass substrates at temperature $T_S = 300$ K. The residual pressure was varied from 10^{-3} to 10^{-6} Pa (oilless evacuation). The film microstructure and phase composition were studied using the transmission electron microscopy (TEM) of high resolution and electron diffraction.

In is found that there is the whiskers growth in Sb amorphous films obtained by slow condensation on face (001) KCl after samples storage at normal conditions during two years in state separated from a substrate. The microdiffractions of whiskers corresponds to a lattice of oxide antimony Sb_2O_4. The whiskers morphology is varied: there are long hairlines (length 2-3 μm; diameter 0,1 μm) and thin plates.

By the observation of high resolution TEM the "globuls" were revealed both on the whiskers vertexes and on their lateral surfaces. It is shown that the whiskers growth begins from a copper net on which the sample was prepared.

This experimental results have confirmed a model of whiskers growth by the scheme of vapour-liquid-crystal, or by the mechanism "VLC".

It was revealed the intensive whiskers growth in $NaSbS_2$ films obtained by PLE. The lines in the electron-diffraction pattern point on the presence of $NaSbS_2$ compounds with parameters of the bulk in cubic packing. The whiskers density in a plane of substrate is $(2{\div}4)\cdot10^4$ sm $^{-2}$. Apparently, such crystallization is due to a strong molecular building anisotropy of ternary compounds.

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LOW TEMPERATURE PROPERTIES OF Si-Ge WHISKERS WITH COMPLEX DOPING

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The present paper deals with a study of Si-Ge whisker resistance in the temperature range 4.2-300K. In the previous papers, e.g. [1], a dependency of resistance on temperature was investigated for the whiskers with various compositions of solid solution. As a rule, a ratio of resistivities $\rho_{4.2}/\rho_{300}$ did not exceed 3.5. In the present paper the parameter $\rho_{4.2}/\rho_{300}$ is shown to be essentially changed at doping of Si-Ge whiskers with various impurities. So, at the whisker doping with B+Au for solid solution composition x=0.3 the parameter consists of 10^4. An exponential character of dependency R(T) with ΔE=0.014 eV is observed in the temperature range 4.2-200K.

$Si_{1-x}Ge_x$ whiskers with x=0.1 were mainly under investigation. For the whiskers doped with Zn+Au the dependency R(T) consists of two exponential regions at 150-200K and 40-60K correspondingly. Impurity activation energy in the temperature region 150-200K is equal to 0.32 eV. For the whiskers doped with Hf+Au (ρ=8.4 Ώ·cm, T=300K) the regions of jump-like change of resistance are revealed at temperature T=25K and T=50K. Besides an increase of the whisker resistance with growth of temperature from 100 to 200K is found. The whiskers are shown to be photosensitive both in photovoltaic an photoresistive regimes. Dimensional dependency of the whisker photoconductivity is observed.

High magnitudes of the whisker resistivity are found at the whisker doping with Pt+$NiCl_2$+Mn (ρ=1.3 Ώ·cm, T=300K). A peculiarity of the whiskers is unlinear I-U characteristics, that at temperature of liquid nitrogen becomes diod-like. On some specimens an investigation of the performancies of Pt/Si-Ge contacts is carried out.

The whiskers doped with such impurities are shown to be used as piezo- and thermoresistors as well as photoconverstors.

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STRUCTURE AND ELECTRONIC PROPERTIES OF $La(Ni,Al)_5$ ALLOYS

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Nanocrystalline and polycrystalline $LaNi_{4.2}Al_{0.8}$ alloys were prepared by mechanical alloying (MA) followed by annealing and arc melting method, respectively. MA and arc melting were performed under high purity argon atmosphere. The bulk and surface chemical compositions of the samples were measured by X-ray fluorescence and Auger photoelectron spectroscopy, respectively. The MA process of the La-Ni-Al mixture has been studied by X-ray diffraction (XRD) and scanning electron microscopy. The X-ray photoelectron spectroscopy (XPS) spectra were measured at room temperature using Al-K_α radiation of 1486.6 eV.

Results on XRD during MA showed that the originally sharp diffraction lines of La, Ni and Al gradually become broader and their intensity decreases with milling time. The powder mixture milled for more than 30 h has transformed completely to the amorphous phase, without formation of an other phase. Formation of the nanocrystalline alloy was achieved by annealing the amorphous material in high purity argon atmosphere at 1020 K for 0.5 h. All diffraction peaks were assigned to those of the hexagonal crystal structure of $CaCu_5$-type. The size of amorphous powder grains was of the order of 50 nm; they have a tendency to agglomerate. The mean crystallite sizes of MA and annealed material were less than 80 nm. The annealing results in grain growth, as was reported earlier in the case of other nanocrystalline ZrV_2-type materials. The mean crystallite sizes of the arc melted and homogenised sample were less than 1000 nm.

XPS studies showed that the shape of the valence band measured for the arc melted (polycrystalline) $LaNi_5$ is practically the same compared to that reported earlier for the single crystalline sample. The substitution of Ni in $LaNi_5$ by Al leads to some modifications of the electronic structure of the polycrystalline sample. For instance, the main Ni-3d structure of the valence band in the $LaNi_{4.2}Al_{0.8}$ is narrower compared to that measured for the $LaNi_5$. The above behaviour is consistent with decrease of Ni-Ni interaction due to lattice expansion associated with the Ni substitution by Al. On the other hand, the XPS valence band of the MA nanocrystalline $LaNi_{4.2}Al_{0.8}$ alloy is considerably broader compared to that measured for the polycrystalline sample. This is probably due to a strong deformation of the nanocrystals. Normally the interior of the nanocrystal is constrained and the distances between atoms located at the grain boundaries expanded. Furthermore, the Al atoms could also occupied metastable positions in the nanocrystals. The strong modifications of the electronic structure of the nanocrystalline $LaNi_{4.2}Al_{0.8}$ alloy could significantly influence on its hydrogenation properties.

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PREPARATION AND MAGNETIC PROPERTIES OF NiO/Co AND $NiO/Ni_{80}Fe_{20}$ BILAYERS

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NiO/Co and $NiO/Ni_{80}Fe_{20}$ (Permalloy) bilayers were prepared at 293 and 420 K onto SiO_2(101)/Si(111) and glass substrates using UHV (5×10^{-10} mbar) RF/DC magnetron sputtering. The Co and Permalloy (Py) layers were deposited using a DC source in an Ar atmosphere. The NiO-layer was prepared using a RF source in Ar + O_2 atmosphere. Typical deposition rate for the Co (Py) and NiO layers was equal to 0.1 and 0.05 nm/s, respectively. After preparation of Si(111) substrate with native SiO_2(101) surface layer we have first deposited NiO layers. The Co (Py) layers were then grown immediately onto the NiO. The top Co (Py) layers had a step-like wedge form. Wedge-shaped layers were grown by steeply moving a shutter in front of the substrate during deposition. Finally, 5 nm - Cu cap layer was deposited to prevent the oxidation of the Co (Py) layer. The chemical composition and the cleanness of all layers was checked *in-situ*, immediately after deposition, transferring the samples to an UHV (4×10^{-11} mbar) analyse chamber equipped with Auger and X-ray photoelectron spectroscopy (AES, XPS). From the exponential variation of the XPS Co-2p, Ni-2p, Fe-2p, and NiO-2p integral intensities with increasing layer thickness we conclude that the Co, Py, and NiO layers grow homogeneously. The structure of the samples was examined *ex-situ* by standard θ-2θ X-ray diffraction with Co-K_α radiation. The thicknesses of individual Co, Py, and NiO layers were determined using X-ray fluorescence analysis (XRF). The magnetic characterisation of the bilayers was carried out at RT using the magnetooptical Kerr effect and a vibrating sample magnetometer (VSM). The coercive and unidirectional anisotropy fields were determined from the in-plane hysteresis loop measurements.

For the Co/NiO bilayers with $d_{Co} > 20$ nm the high-angle X-ray diffraction patterns show an appreciable (111) texture of fcc Co and NiO. The average Co and NiO crystallite sizes in direction perpendicular to the substrates, determined from the Scherrer equation, are comparable to their respective sublayer thicknesses. The peak positions and shape of the AES and XPS spectra revealed formation of the single phase NiO layer during the reactive RF sputtering. Results on ex-situ magnetic measurements showed that the unidirectional anisotropy field is inversely proportional to the Co (Py) layer thickness down to 2nm. A maximal RT coupling energy for the NiO-Co and NiO-Py interface was estimated as 0.05 and 0.04 mJ/m^2, respectively, for the samples prepared at 420 K onto SiO_2(101)/Si(111) substrates. The magnetisation of the bilayers was described by a simple model with nonmagnetic ("dead") Co (Py) ultrathin layer at the NiO-Co (NiO-Py) interface. We have estimated a minimal nonmagnetic Co and Py thickness as 0.04 and 0.06 nm, respectively, for the bilayers prepared at 420 K onto SiO_2(101)/Si(111) substrates. The above behaviour could be explained by the greater roughness and/or interdiffusion at the NiO-Co (NiO-Py) interface for the samples prepared at 293 K onto glass substrates.

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COULOMB CORRELATION EFFECTS ON TUNNEL AGNETORESISTANCE IN MESOSCOPIC JUNCTIONS

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Electric current flowing through an atomic-like level of an impurity (quantum dot) embedded in the barrier between external electrodes in a ferromagnetic tunnel junction is considered theoretically in the sequential tunneling limit. The effects due to Coulomb correlations are studied for parallel and antiparallel orientation of the magnetic moments of external electrodes. Master equation method is applied to calculate the average level occupation numbers, electric current and tunnel magnetoresistance (TMR) for selected values of the correlation parameter U. Apart from this, a few special cases in the large U limit are analysed in detail. Numerical results show that Coulomb correlations can suppress electric current in a certain voltage range, which takes place for a certain asymmetry between spin polarisations of the external electrodes and for asymmetrical distribution of impurities within the barrier. It is also shown that strong Coulomb correlations lead to an enhanced TMR.

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