CZECH TECHNICAL UNIVERSITY
IN PRAGUE

DOCTORAL THESIS STATEMENT

Czech Technical University in Prague

Faculty of Nuclear Sciences and Physical Engineering

Department of Solid State Engineering

Anna Lynnyk

Spectroscopic Ellipsometry -temperature dependent studies of crystals and thin films

Ph.D. programme: Applied Natural Sciences
Branch of study: Physical Engineering

Doctoral thesis statement for obtaining the academic title of "Doctor", abbreviated to "Ph.D."

Prague, 2015

The doctoral thesis was produced in full-time manner. Ph.D. study at the department of Solid State Engineering of the Faculty of Nuclear Sciences and Physical Engineering.

Candidate: Mgr. Anna Lynnyk
Institute of Physics
Czech Academy of Sciences
Na Slovance 2, 182 21, Prague 8

Supervisor: prof. Ing., Zdenek Bryknar, CSc.
Department of Solid State Engineering
Faculty of Nuclear Sciences and Physical Engineering
Brehova 7, 115 19, Prague 1

Technical supervisor: Ing. Alexandr Dejneka, Ph.D.
Institute of Physics
Czech Academy of Sciences
Na Slovance 2, 182 21, Prague 8

Opponents:

prof. RNDr. Miroslav Hrabovsky, Dr.Sc.

doc. RNDr. Vitezslav Stranak, PhD

The doctoral thesis statement was distributed on:.........

The defence of the doctoral thesis will be held on .... at .....a.m./p.m. before the Board for the Defence of the Doctoral Thesis in the branch of study of Physical Engineering in the meeting room No. ....of the Faculty of Physical Engineering of the CTU in Prague.

Those interested may get acquainted with the doctoral thesis concerned at the Dean Office of the Faculty of Nuclear Sciences and Physical Engineering, at the Department of Solid State Engineering, Brehova 7, 115 19, Prague 1.

Prof. Ing. Stanislav Vratislav, CSc.
Chairman of the Board for the Defence of the Doctoral Thesis in the branch of study of Physical Engineering Faculty of Nuclear Sciences and Physical Engineering of the CTU in Prague
Brehova 7, 115 19, Prague 1

Abstract

This work is mainly focused on the sophisticated temperature dependent measurements, which extended the possibilities of ellipsometry and made it possible to investigate optical spectra as a function of temperature. This made the ellipsometry method perfectly suited for the experimental investigations of the electronic excitations and their relation to the ordering phenomena in oxides. For this research the well-known perovskite materials were chosen: model ABO_3 perovskite $SrTiO_3$ and $KTaO_3$ single crystals, films of $PbZr_xTi_{1-x}O_3$, widely used in microelectronics [2, 3, 4, 5], lead-free $Ba_{0.4}Sr_{0.6}TiO_3$ [6, 44] and $NaNbO_3$ films. Ellipsometry was used to update and optimize the data of phase transitions in these materials by means of the characteristic strong changes in the optical properties.

Ellipsometry appeared to be the suitable method for crystal surface phase transition detection, shown on $SrTiO_3$ crystal.

The attempt of explaining the negative thermooptics in $SrTiO_3$ and $KTaO_3$ single crystals (the model ABO_3 perovskites) was given in this work. By means of ellipsometry we established the so called "soft electronic band" which became evident from the shift of the edge of the direct interband optical transitions to the lower energies at cooling.

The complex relationship between the strain and polarization in perovskites was investigated on the $PbSc_{0.5}Nb_{0.5}O_3$ relaxor ferroelectric epitaxial thin films, a new promising technologically important material. The ellipsometry study allowed us to obtain the new interesting results, which contribute to the general understanding of the perovskite nature.

Perovskite $SrTi_{1-x}Mn_xO_3$ nanopowders were synthesized in our laboratory in order to achieve and study the new properties concerning the dimensional effects and doping in perovskites.

Abstract

Tato práce je zaměřena na výzkum teplotní závislosti optických vlastností některých perovskitových materiálů metodou spektrální elipsometrie. Teplotně závislá elipsometrícká měření podstatně rozšiřují možnosti této metody a umožnují tak výzkum elektronových excitací a jejich souvislost s uspořádáním ve zkoumaných oxidech. Pro tento výzkum byly zvoleny dobře známé perovskitové materiály: modelové ABO_3 mono krystaly $SrTiO_3$ a $KTaO_3$, vrstvy $PbZr_xTi_{1-x}O_3$, široce používané v mikroelectronice [2, 3, 4, 5], bezolovnaté $Ba_{0.4}Sr_{0.6}TiO_3$ [6, 44] a $NaNbO_3$ vrstvy.

Elipsometrie byla použita pro aktualizaci a optimalizaci dat fázových přechodů v těchto materiálech pomocí charakteristických změn optických vlastností. Ellipsometrie je také vhodnou metodou pro zkoumání fázových přechodů na povrchu krystalu, což je demonstrováno na krystalu $SrTiO_3$.

Jedna z kapitol této práce je zaměřena na objasnění negativního termooptického jevu v krystalech $SrTiO_3$ a $KTaO_3$. Metodou spectrální elipsometrie byla určena dielectrická funkce a její teplotní závislost. Z posuvu absorpční hrany k nižším energiím při snižování teploty bylo možno určit tzv. "měkké elektronové pásy", charakteristické pro tyto materiály.

Komplexní vztah mezi pnutím a polarizací v perovskitech byl zkoumán na relaxorových ferroelektrických epitaxních tenkých vrstvách $PbSc_{0.5}Nb_{0.5}O_3$. Je to nový slibný technologicky důležitý materiál. Elipsometrie nám umožnilá získat nové zajímavé výsledky, které přispívají k pochopení materiálů s perovskitovou strukturou.

Pro studium nových vlastností týkajících se rozměěrových efektů a vlivu dopování na vlastnosti perovskitů byly v naší laboratoři připraveny nanoprášky $SrTi_{1-x}Mn_xO_3$.

Current situation of the studied problem

Spectroscopic ellipsometry is a highly sensitive optical technique which enables to investigate the complex refractive index of thin films and bulks in the wide spectral range giving access to other fundamental physical parameters (crystalline structure, polarization, surface roughness etc). Optimization of ellipsometry for the study of various structural phase transitions in solids would be a very perspective direction of using this method for fast diagnosis of the materials used in microelectronics. By means of relatively simple in application ellipsometry it is possible to detect phase transitions or other structural perturbations even for ultra-thin films while the use of other techniques is impossible or very complicated in this case. The possibility and limitation of using of such parameters as band gap energy, refractive index and surface roughness, for phase transition detection on different examples of perovskite oxides need to be estimated. The following materials were chosen for this purposes:

- $PbZr_xTi_{1-x}O_3$ thin films (PZT) is a functional material, widely used in micro systems technology [2, 3, 4], particulary, for memory, piezoelectric and pyroelectric devices as it provides a direct electro-mechanical coupling [5].

- $Ba_{0.4}Sr_{0.6}TiO_3$ is a promising material for a number of applications such as high dielectric constant capacitors, non-volatile memories with low switching voltage, infrared sensors and electro-optic devices such as planar waveguides or optical switches and tunable microwave systems [6].

- $NaNbO_3$ - piezoelectric material [7] for potential application in surface acoustic wave, optical wave guiding, and frequency doubling devices [7, 8, 9, 10], capable to work at the extreme conditions such as high temperatures.

- Surface phase transitions were studied on $SrTiO_3$ crystals. Except of that task this crystals together with the $KTaO_3$ ones were used as the model of ABO_3 perovskites for study negative thermooptics in these materials. Ellipsometry gives the possibility of study of the band gap changes under the temperature influence. So the "soft electronic modes", predicted by Pisarev in 1986 [1] became "detectable" by this technique.

- $PbSc_{0.5}Nb_{0.5}O_3$ epitaxial relaxor ferroelectric thin films is a technologically important material for transducers and ceramic capacitors in the electronic industries also presenting an interesting theoretical problem. The changes of optical properties in thin relaxor ferroelectric films with decreasing film thickness and effects imposed on these properties by epitaxial growth are poorly explored.

The ellipsometry study of these materials allowed to obtain the new results that contributed to the general understanding of the perovskite nature.

The other part of the work was devoted to the properties of the mentioned above perovskite $SrTiO_3$ in nano scale state. Recently the properties of doped incipient ferroelectrics become the object of intensive study. Particularly, it was observed some new and intriguing properties of $SrTi_{1-x}Mn_xO_3$, like the polarization response, low-temperature dielectric relaxation, polar behavior and magnetoelectric multiglass properties in lightly Mn doped STO [11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. Moderately and heavily Mn-doped STO is considered lately as a new magnetic, semiconducting, multiferroic and "spintronic" material. The growing of heavily Mn doped crystal with preserving of the cubic perovskite-type structure demands the special conditions, such as high-pressure and annealing in oxygen [21]. The cheaper and easier way of getting the "perfect" material which can host a larger amount of a doping element than the same bulk material is the synthesis of nanopowders, because the materials, which are unstable in bulk, can often be obtained in the form of nanoparticles [22, 23, 24]. This circumstance opens a grate possibilities for getting the new materials with intriguing properties.

Aims of the doctoral thesis

- Optimization of ellipsometry for the study of various structural phase transitions in solids. Basing on the theoretical background of Fridkin's theory [32], estimation of the possibility and limitation of using of band gap energy, refractive index and surface roughness, for phase transition detection on different examples of perovskite oxides: thin films of $PbZr_xTi_{1-x}O_3$ made by various preparation methods, $Ba_{0.4}Sr_{0.6}TiO_3$, $NaNbO_3$ and $SrTiO_3$ single crystals.
- Detailed ellipsometry study of optical properties in a wide spectral and temperature regions of the $SrTiO_3$ and $KTaO_3$ model single crystals with the purpose of understanding of the nature of the negative thermo-optic effect.

- Thermooptical study of the epitaxial relaxor ferroelectric films of $PbSc_{0.5}Nb_{0.5}O_3$ in order to elucidate a complex relationship between strain and polarization in perovskites.
- Synthesis of the heavily Mn-doped cubic perovskite $SrTi_{1-x}Mn_xO_3$ nanopowders using the citrate sole-gel method and investigation of the new properties appeared in perovskites with the decreasing of size and doping.

Methods used in the work

The main method used in this work is Ellipsometry. It is an optical technique for investigating the dielectric properties of the material. In this method the elliptical polarization of light is used and the achieved information is a function of wavelength or energy (spectra). The measured signal in ellipsometry is the change in polarization of the incident radiation as it interacts with the material structure. This signal depends on the thickness as well as the materials properties, so ellipsometry can be a universal tool for contact free determination of thickness and optical constants of films of all kinds [25], which made this method applicable in many different fields: for semiconductor physics as well as for microelectronics and biology, for basic research as well as for industrial applications [26, 27, 28, 29, 30]. Ellipsometry is very sensitive to the change of the optical response of the incident radiation interacting with the sample so the promising field of ellipsometry application is phase transitions detection. Optical measurements in this work were performed on the J. A. Woollam variable angle spectroscopic ellipsometer operating in rotating analyzer mode. The main ellipsometric angles Ψ and Δ were measured in the spectral range of 250-1200 nm at the incidence angles of 65, 70 and 75 degrees at room temperature. For the high temperature measurements specially designed sample holder with PC-controlled heating element was used. Low temperature measurements were performed with the Janis liquid helium cryostat at one angle of incidence (70°). The thermocouple was mounted at the surface of the sample. Such configuration allowed us to achieve the accuracy more than 0.5 K. The heating/cooling rate was 1-3 K/min. Temperature dependences were measured in two ways: 1) Angles Ψ and Δ were measured as a function of the wavelength at fixed temperatures. 2) Dynamic scan of Ψ and Δ at several fixed wavelengths was performed. First type of measurements gave us the temperature dependence of n and k dispersion and optical band gap, and the second one allowed us to obtain the temperature dependence of n and k at fixed wavelengths. The fixed wavelengths were chosen experimentally to increase the sensitivity of SE measurements to any phase transitions and structural changes. In the most cases it is enough to take some wavelength near the absorption edge because any structural changes give a considerable contribution to the interband transitions which can be seen in the refraction and absorption indices changing [31]. Simple model was used to fit room temperature and thermo-ellipsometric data: substrate/film/roughness. The surface roughness was calculated as an effective medium approximation (EMA) [26]. In the case when anisotropy, inhomogeneity and defects of the films and crystals were not taken into account the calculated values are called as "effective". Experimental data were analyzed with the software package WVASE32.

The main contribution of the thesis

Spectroscopic ellipsometry applied to phase transitions in solids

CSD and SP $PbZr_xTi_{1-x}O_3$ thin films

In our experiments a real-time measurements of the main ellipsometric angles during sample heating and cooling were carried out. PZT materials prepared with different technologies (CSD (chemical solution deposited) and SP (planar multitarget reactive sputtered)) possess the different stoichiometry [3]. From the temperature dependence of the optical energy gap took at the constant absorption coefficient of $\alpha = 1000 cm^{-1}$ it was established four linear intervals, which according to the Fridkin's theory [32, 33] was possible to attribute to different phases of the PZT material. A band gap discontinuity at the *phase I* $\rightarrow$ *phase II* transition for the CSD PZT indicated a first-order phase transition. It can be concluded that the spectroscopic ellipsometry allowed to obtain three important temperature points for self-polarized CSD and SP PZT films in the range from room temperature to $500°C$. These temperatures are $200°C$, $290°C$ and $400°C$. The point of the ferroelectric/paraelectric phase transition is the last one.

By means of the of spectral ellipsometry the nature of phase transitions in PZT prepared with different technologies can be understood deeply. These data will profit for improvement of the preparation technology and the obtainment of PZT films with given properties.

$Ba_{0.4}Sr_{0.6}TiO_3$ thin films

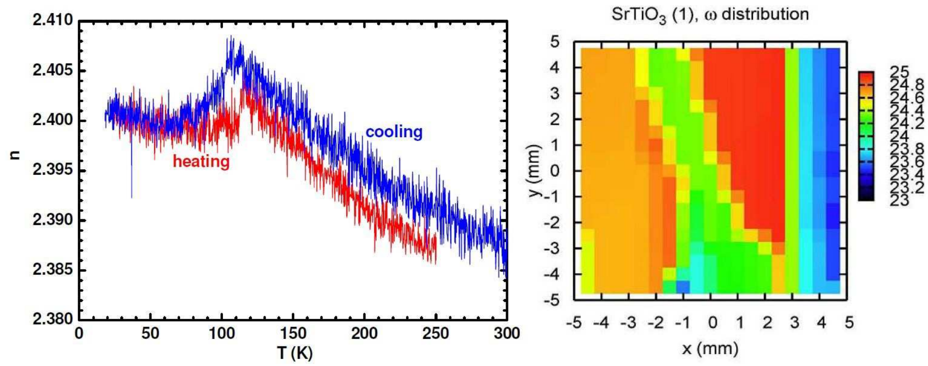
By means of ellipsometry it was possible to optimize the data on the optical, structural, and dielectric properties of $Ba_{0.4}Sr_{0.6}TiO_3$ films which depend substantially on the preparation method, composition, film thickness, grain size, and annealing. In our experiments the characteristic strong changes in the refraction index as well as the direct changes in the main ellipsometric angles Ψ or Δ for some films, were achieved and discussed. In comparison with BST ceramics or unstressed films (the phase transitions for this BST composition should be at about $190, 250$ and $320\ K$), the achieved temperatures of these transitions appeared to be shifted to the lower values. This difference could be caused by the tensile stresses, inhomogeneity and defects within the film and interfaces.

$NaNbO_3$ thin films

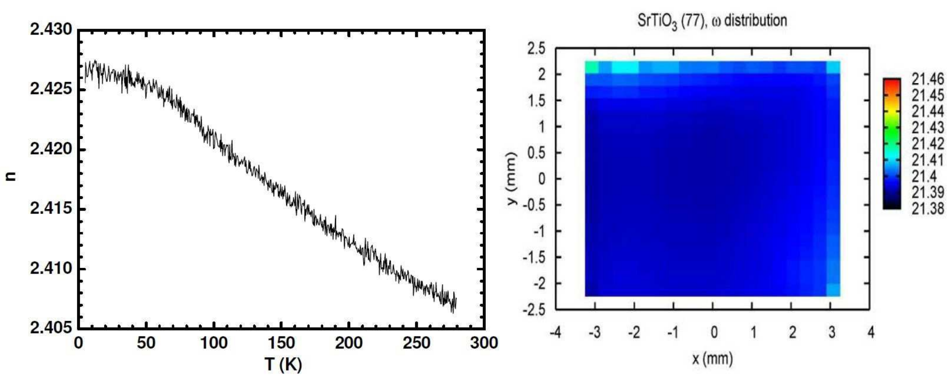
Sodium niobate $NaNbO_3$ (NN) possess the most interesting complex sequence of phase transitions (6 in sum in the film state) among the all perovskites, in the temperature range of -80 to $+650°C$ changing its phase from high-temperature paraelectric to antiferrodistortive and then antiferroelectric phase at $+638°C$ [34]. It posses the notable piezoelectricity [7], large electro-optic coefficient, high-temperature ferroelectricity, moderate dielectric constant and excellent photorefractive properties. The films of $NaNbO_3$ had the thickness gradient. So in our calculations we used the effective refractive index n_{eff}, which can be defined for a fictive isotropic medium by averaging the same ellipsometric parameters Ψ, Δ obtained experimentally. The achieved data of extremes in refractive index mainly coincided well with existing one on phase transition temperature (the temperatures of 643, 718, 776, 793 and 805 K). Spectroscopic ellipsometry was demonstrated as an effective method for phase transition investigation in $NaNbO_3$ thin films.

$SrTiO_3$ single crystals: Influence of crystal surface defects on thermo-optical properties and phase transition behavior

In this experiment ellipsometry was applied together with the X-ray omega scan technique for exploring the surface of high quality Verneuil and TSS grown $SrTiO_3$ single crystals. We were interested on the antiferrodistortive phase transition at 105 K. The refractive index at the wavelength $\lambda = 600\,nm(2.1\,eV)$



(a)



(b)

Figure 1: Refractive index at 600 nm (left) and XRD surface omega-scan distribution (right) from (100) surface of Verneuil Crystal GmbH grown $SrTiO_3$ (a), from (110) surface of Mateck TSSG grown $SrTiO_3$ single crystal (b)

was measured in the temperature range of $4.2 - 300\ K$. For the Verneuil crystal the huge jump in the value of n near the phase transition temperature (Fig. 1a) appeared at about 20 degrees higher value than phase transition point [35, 36]. The X-ray omega scan revealed the disoriented blocks on the surface of the crystal, which could be the reason of the temperature shift as these blocks may cause the local stress near the surface, bringing the distortions connected with the order parameter [37]. The surface of TSSG crystal appeared to be perfect, with-

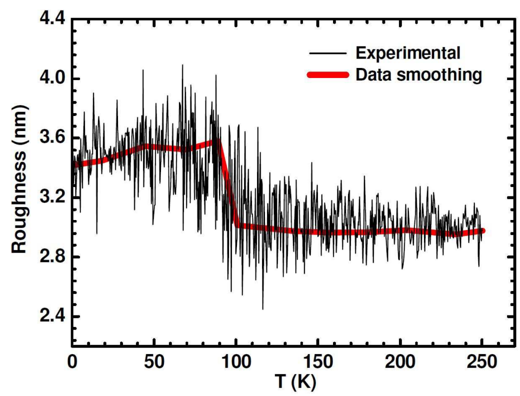
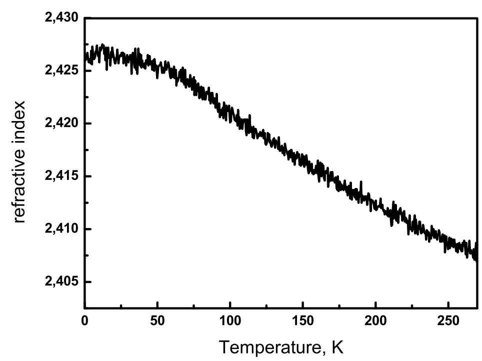


Figure 2: Surface roughness as a function of the temperature for Mateck TSSG grown $SrTiO_3$ single crystal [38].

out disoriented blocks, with $n(T)$ dependence (Fig. 1b) very close to that of the bulk, measured by spectrophotometry. No jumps or other evidence of phase transition is revealed except for the jump, detected in the surface roughness, see Fig. 2. So it was possible to conclude, that the physical reason for such changes in the surface roughness is the structural changes of the surface under a second order antiferrodistorsive cubic-tetragonal $O_h^1 \rightarrow D_{4h}^{18}$ structural transition. Ellipsometry is accurate enough for measuring the phase transitions, followed by small structural differences. This method possesses the high sensitivity to any global and local structural changes, and in the case of thin films and it is not possible to separate the phase transition taking place in the whole film from the surface or interface phase transition. Therefore, phase transitions for films was observed at temperatures different from those detected for single crystals. In this occasion, additional methods of the phase transitions study like specific heat measurements and x-ray would be necessary.

A "soft electronic band" and the negative thermooptic effect in strontium titanate and potassium tantalat

There are some basic properties of $SrTiO_3$ and $KTaO_3$ about which little is known, and their nature remains unclear. One such property is the "negative thermo-optic effect" (TOE) in this materials, which consists of an increase in the refractive index in the transparency range upon cooling ($dn/dT < 0$). This



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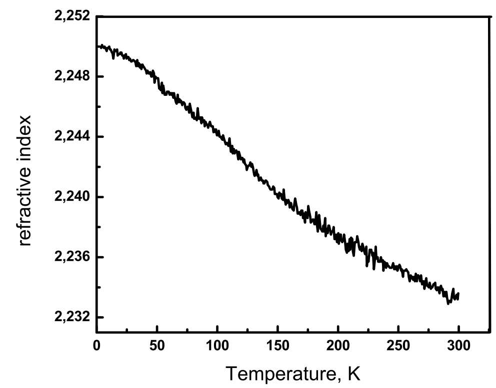

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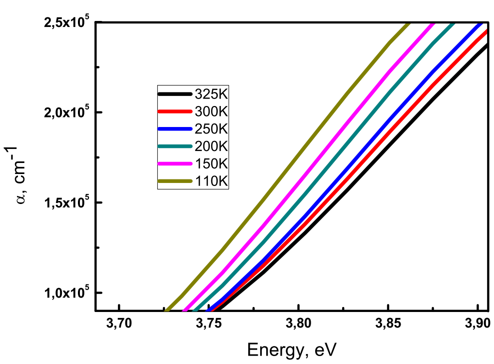

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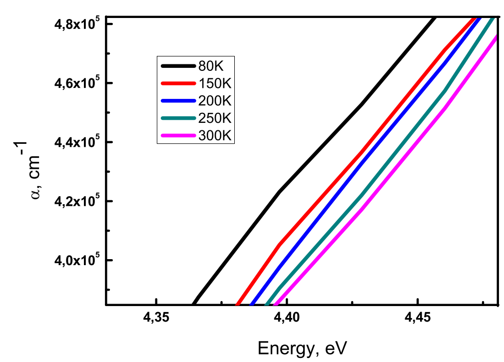

(d)

Figure 3: Temperature dependence of the refraction index of $SrTiO_3$(a) and $KTaO_3$ (b) single crystals refractive index taken at wavelength 600 nm, the part of absorption coefficient spectra corresponding to the direct optical transitions for $SrTiO_3$ (c) and $KTaO_3$ (d) crystals at different temperatures.

behavior greatly differs from that known for conventional ionic crystals and semiconductors, in which the "positive thermo-optics" coefficient is mostly connected to the red shift of the band edge optical transitions with temperature [39, 40, 41], with the exception of special cases such as graphene and narrow-band A_4B_6 compounds [42, 43]. The "proper" temperature effect which does not depend on temperature dilatation is considered to be connected with isochoric electron-phonon interaction and cause the variation of the refraction. The spectral ellipsometric studies of the optical properties of $SrTiO_3$ and $KTaO_3$ crystals over broad spectral (1-6 eV) and temperature (80-300 K) regions were performed in order to elucidate the nature of the negative TOE in this crystals. The new data on the refraction index behavior and near band-edge transitions controlling reflection in the visible region and their temperature evolutions were presented. It was shown that whereas the indirect transitions lowest in energy shift to higher energies on cooling, the energy of the stronger direct optical transitions in the region of $3.7-4.0\ eV$ for $SrTiO_3$ shifts to the opposite side, to lower energies, and these transitions can be treated as the "soft electronic band" predicted in [1]. It is concluded that the presence of this "soft electronic band" together with increasing absorption band intensity at 4.8 eV results in the increase of the refractive index on cooling, elucidating the origin of the negative proper thermooptics in $SrTiO_3$. For $KTaO_3$ the similar tendency was noticed: the absorption edge in the region of the lowest indirect ($R \rightarrow \Gamma$) optical transitions, $3.7-4.2\ eV$, was observed to shift to the lower energies upon cooling. Simultaneously, an increase and "blue shift" of the optical absorption in the region of the direct $X_{5'upper} \rightarrow X_3$ transitions ($4.3-4.8\ eV$) were observed, which should be responsible for the nature of the appropriate negative thermo-optics in this material. The similarity of the refractive index behavior of $KTaO_3$ and $SrTiO_3$ crystals hints that negative thermooptics is common for incipient ferroelectrics.

Thermo-optical studies of epitaxial perovskite-structure relaxor ferroelectric $PbSc_{0.5}Nb_{0.5}O_3$ thin films

In this work ellipsometry was used for determining of the optical constants of the epitaxial perovskite-structure relaxor ferroelectric $PbSc_{0.5}Nb_{0.5}O_3$ films with thickness of $10-50\ nm$ in broad spectral and temperature ranges. The films possess a metrically tetragonal crystal structure with a biaxial in-plane compressive strain of $0.1\% - 0.8\%$. It was shown that various strain conditions lead to the dramatic changes in the spectra of the optical constants (see Fig. 4). The characteristic energies of the spectra, including the band gaps, vary by $0.1 - 0.5\ eV$. Thermo-optical studies evidenced a frustration of the ferroelectric phase transition. A complex relationship between strain, polarization, and optical properties in metrically tetragonal $PbSc_{0.5}Nb_{0.5}O_3$ films is explored by means of thermo-optic approach.

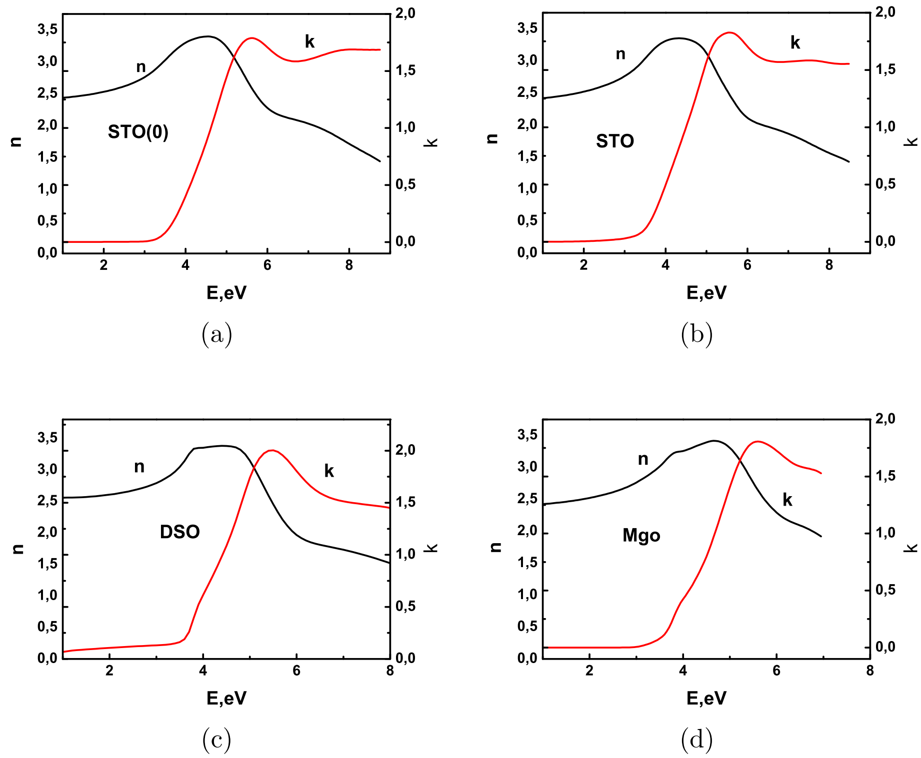

Figure 4: The optical constants determined as a function of photon energy E at room temperature in the PSN films grown on (a) and (b) $SrTiO_3$, (c) $DyScO_3$, and (d) MgO substrates at the deposition temperature of (a) 873 K and (b)-(d) 973 K.

Structure and composition of $STO : Mn$ nanopowders

The single-phase $SrTi_{1-x}Mn_xO_3$ nanoparticles were successfully fabricated in this work, using the citrate sol-gel method. The amorphous gel-like $TiO_2 * xH_2O$ precipitate was achieved by hydrolyzation of $C_{12}H_{28}O_4Ti$ (Fluka) (a liquid tetrapropyl orthotitanate) with water and then with NH_4OH, a concentrated solution of ammonia. Then a citrate titanium complex solution was achieved by washing and dissolving of this precipitate in citric acid ($C_6H_8O_7$). The concentration of Ti in this solution was determined gravimetrically. Then the manganese nitrate solution $Mn(NO_3)_2 * 4H_2O$ with a controlled quantity of Mn and a strontium nitrate $Sr(NO_3)_2$ (both Sigma-Aldrich) were mixed together; citric acid in the quantity of 4:1 and ethyleneglycol in proportion of 8:1 toward to Sr were added to the solution. The polymeric gel from this solution was formed during heating at $100°C$, and after that the organic part was burned away at $600°C$ in air. The additional annealing was performed at $1000°C$ in air atmosphere in order to enhance the crystallinity. For both temperatures an annealing time of 1 hour was chosen. Kinetics was facilitated by small particle size and high surface area so all chemical transformations related to phase composition were expected to take place within the first annealing hour. The resulting powder was yellow or tinted green with low amounts of Mn ($x \leq 20 - 30\%$ with respect to Ti), and it became brown (black for $1000°C$ annealing conditions) when the Mn content was above 30 $mol\%$. Complex investigation using XRD, PIXE, SEM and Raman scattering have been done. It was revealed that $SrTi_{1-x}Mn_xO_3$ nanopowders have the structure of the room-temperature cubic perovskite with Mn^{4+} substituting the octahedral Ti^{4+} ion. The influence of thermal annealing and Mn-dopant concentration on the nanoparticle size, nanopowder composition, and the lattice constant have been studied. Regardless of the annealing temperature, all compounds containing the 40 $mol\%$ of Mn revealed a single-cubic perovskite structure. Hexagonal $SrMnO_3$ at $x = 0.5$ appeared after the particle growth from 10 to 40 nm after annealing at $1000°C$. Fragments of the non-reacted $SrCO_3$, Mn_3O_4 or hexagonal $SrMnO_3$ appeared at $x \geq 0.5$. The $SrTiO_3$-like perovskite as a major phase with some admixture of Mn-containing phases of hexagonal $SrMnO_3$ and/or Mn_3O_4 is performed in the more concentrated powders of $SrTi_{1-x}Mn_xO_3$. The lattice constant monotonically decreases as the Mn concentration increases up to

$x = 0.5$, following Vegard's law. The sizes of the nanoparticles decrease as well with the Mn content. The structural transformations occur in the heavily concentrated $SrTi_{1-x}Mn_xO_3$ nanopowders. This phenomenon was proved by the activation of the polar Last TO_2 optical mode, during the Raman scattering investigation performed at $T = 10$ K. This aspect was tentatively attributed to the possible polar phase formation, induced by the off-center displacement of the Mn^{4+} octahedral ions (with non-zero d orbitals) at the formation of a strong $Mn-O$ covalent bond. The magnetic susceptibility study suggests that magnetic clustering in the $SrTi_{1-x}Mn_xO_3$ nanopowders happen at a low-temperature. The low-temperature transition to a polar phase in the heavily doped $SrTi_{1-x}Mn_xO_3$ nanopowders, discovered in this work, allows to refer this material to the multiferroic one.

Conclusions

- It was shown in this research that spectroscopic ellipsometry is a very powerful technique for the study of phase transitions in thin films and crystals. The possibility of detection and study of the surface phase transitions by spectroscopic ellipsometry is of great significance from the fundamental point of view as well as from the technological one.
- A detailed spectral ellipsometric study of optical properties in wide spectral and temperature regions of the $SrTiO_3$ and $KTaO_3$ model single crystals was performed in this work. It was concluded that the origin of the negative proper thermooptics in this materials lies in the presence of "soft electronic band". This result is the first step in understanding of the microscopic nature of negative thermooptics.
- Ellipsometry technique was applied for the investigation of the complex relationship between the strain and polarization in the metrically tetragonal epitaxial relaxor ferroelectric $PbSc_{0.5}Nb_{0.5}O_3$ films. The relationship between the strain and the optical properties was found to be more complex than a simplified combination of strain and polarization effects. In addition, the absence of direct correlation between the strain and the polarization and the absence of the ferroelectric transition was observed. These results give the new insight to the physics of the strained systems.

- Additional research was done in the field of nanoparticles. Heavily Mn-doped perovskite $SrTi_{1-x}Mn_xO_3$ nanopowders with a particle size of $10 - 80$ nm and $x = 0 - 0.5$, which exceeds the Mn incorporation limit, were synthesized in this work. The obtained results are very helpful for understanding of the physics of perovskite structure.

List of candidate's works relating to the doctoral thesis

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