

**TALLINNA TEHNIKAÜLIKOOL
KEEMIA JA MATERJALITEHNOLOOGIA TEADUSKOND
MATERJALITEADUSE INSTITUUT**

**TEADUSE- JA
ARENDUSTEGEVUSE
AASTAARUANNE 2014**

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Kinnitan

Marit Kauk-Kuusik, direktori kt.
29.01.2015

tuginedes instituudi nõukogu seisukohtadele

KEEMIA JA MATERJALITEHNOLOOGIA TEADUSKOND
MATERJALITEADUSE INSTITUUT
TEADUS- JA ARENDUSTEGEVUSE AASTAARUANNE 2014

1. Instituudi struktuur

TTÜ Materjaliteaduse instituut, Department of Materials Science,
direktori kt. **Marit Kauk-Kuusik**

Materjaliteaduse instituudi koosseisu kuuluvad:

- Pooljuhtmaterjalide tehnoloogia õppetool, Chair of Semiconductor Materials Technology, **Enn Mellikov**
- Füüsikalise keemia õppetool, Chair of Physical Chemistry, **Andres Öpik**
- Keemiliste kiletehnoloogiate teaduslaboratoorium, Laboratory of Thin Film Chemical Technologies, **Malle Krunks**

2. Materjaliteaduse instituudi teadus- ja arendustegevuse (edaspidi T&A) iseloomustus

2.1 Pooljuhtmaterjalide õppetool /Chair of semiconductor materials – prof. E. Mellikov

Monoterapulber tehnoloogia uurimisgrupi teadustöö kirjeldus (inglise keeles), M. Altosaar/ M. Kauk-Kuusik

The aim of the research is the development of low-cost absorber materials and technologies for photovoltaics. The fundamental research is addressed to new type absorber materials ($\text{Cu}_2(\text{Zn,Cd})\text{SnS}_4$, $\text{Cu}_2\text{Zn}(\text{Ge,Sn})\text{Se}_4$, $\text{Cu}_2\text{ZnSn}(\text{S,S})_4$, SnS) as well as to the development of monograin layer (MGL) solar cells based on these absorbers. Outcomes of this research gave improved understanding of the optoelectronic properties of this promising class of compound semiconductors, their point defects and recombination mechanisms, formation and crystallization processes. Gained knowledge will be used in further developments of synthesis process of monograins, post-growth treatments, and improvements of the device structure and the performance of the kesterite based MGL solar cells.

The main activities in the field of monograin powder studies in year 2014:

- Determination of synthesis conditions and growth mechanisms in the systems of $\text{Cu}_2\text{ZnSnSe}_4$ –KI, $\text{Cu}_2\text{ZnSnSe}_4$ –NaI, $\text{Cu}_2\text{ZnSnS}_4$ –KI and $\text{Cu}_2\text{ZnSnS}_4$ – CdI_2 for monograin powder growth.

- Determination of chemical reactions between precursor materials for $\text{Cu}_2\text{ZnSnSe}_4$ and between precursor materials and used fluxes (NaI, KI) and calculations of reaction enthalpies.
- Preparation and properties of $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ solid solutions synthesized in two different salts (KI, CdI_2) with the aim to optimize the optical band gap of these compounds for absorbers materials in solar cells.

Uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused/The main results:

- It was found, that the growth of $\text{Cu}_2\text{ZnSnSe}_4$ monograin powder crystals in KI involves two prevailing mechanisms: mass diffusion through the liquid phase and sintering of grains. As novelty, the values of $\text{Cu}_2\text{ZnSnSe}_4$ crystals growth parameters $n = \sim 4$ (the geometric factor) and the activation energy of linear crystal growth $\Delta E_d = 0.59 (\pm 0.13)$ eV were determined for the description of crystal growth in KI by formula: $d_m \sim t^{1/n} \exp(-E_d/kT)$.
- It was found, that the chemical formation of $\text{Cu}_2\text{ZnSnSe}_4$ occurred mainly in the molten phase of used salt. XRD and Raman analyses confirmed that the formation of CZTSe started already at 380 °C after the melting of Se that deliberated from the transformation of CuSe to $\text{Cu}_{1.8}\text{Se}$, and then the CZTSe formation process impeded to a great extent due to the presence of solid NaI (KI). After the melting of NaI (KI), the formation of CZTSe was completed. The formation enthalpy of $\text{Cu}_2\text{ZnSnSe}_4$ in NaI was determined experimentally for the first time as -36 ± 3 kJ mol⁻¹ at 661 °C.
- It was found that Cd incorporated into $\text{Cu}_2\text{ZnSnS}_4$ by using CdI_2 as flux and forms the $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ solid solutions with limited content of Cd. Cd concentration increased with increasing synthesis temperature. The activation energy of Cd incorporation was determined as 17.5 ± 2 kJ/mol. It was proposed that the incorporation of Cd atoms takes place at the Zn atom sites and amount of substitutions depends on the Cu/Sn concentration ratio. The route of Cd incorporation into CZTS from CdI_2 was described by the formation of CdI_2^+ complexes in the molten phase of cadmium iodide.
- We confirmed the existence of a complete solid solution series between kesterite-type $\text{Cu}_2\text{ZnSnS}_4$ and stannite-type $\text{Cu}_2\text{CdSnS}_4$ compounds. Structural analysis indicated that the phase transition from kesterite to stannite crystal structure occurred in the solid solutions, where Cd substitutes Zn about 40% ($x=0.4$). In the region $0 < x < 0.4$ the incorporation of Cd into the CZTS decreased linearly the values of band gap from 1.55 to 1.4 eV, while the A_1 Raman mode shifted from 338 to 332 cm⁻¹ and PL band position from 1.3 to 1.1 eV. Subsequent increasing of Cd content did not change these values significantly. The results suggested that $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ solid solution with x around 0.4, having bandgap 1.41 eV, is optimal for absorber layer in single junction solar cells.

Uurimisgrupi olulisemad publikatsioonid aruandeaastal:

1. I. Leinemann, W. Zhang, T. Kaljuvee, K. Tõnsuaadu, R. Traksmäa, J. Raudoja, M. Grossberg, M. Altosaar, D. Meissner, $\text{Cu}_2\text{ZnSnSe}_4$ formation and reaction enthalpies in molten NaI starting from binary chalcogenides. ***Journal of Thermal Analysis and Calorimetry***: Volume 118, Issue 2 (2014) Page 1313-1321

2. I. Leinemann, K. Timmo, T. Kaljuvee, K. Tõnsuaadu, R. Traksmäa, M. Altosaar, D. Meissner, Reaction enthalpies of $\text{Cu}_2\text{ZnSnSe}_4$ synthesis in KI. *Journal of Thermal Analysis and Calorimetry*, accepted for publication 02.12.2014.
3. G. Nkwusi, I. Leinemann, J. Raudoja, V. Mikli, M. Kauk-Kuusik, M. Altosaar, E. Mellikov, Synthesis of $\text{Cu}_2(\text{Zn,Cd})\text{SnS}_4$ Absorber Material for Monograin Membrane Applications. In: *MRS Proceedings* 1638, (2014) <http://dx.doi.org/10.1557/opl.2014.245>
4. M. Pilvet, M. Kauk-Kuusik, M. Altosaar, M. Grossberg, M. Danilson, K. Timmo, A. Mere, V. Mikli (2014). Compositionally tunable structure and optical properties of $\text{Cu}_{1.85}(\text{Cd}_x\text{Zn}_{1-x})_{1.1}\text{SnS}_{4.1}$ ($0 \leq x \leq 1$) monograin powders. *Thin Solid Films*, xx - xx. In Press, Corrected Proof (2014) <http://dx.doi.org/10.1016/j.tsf.2014.10.091>

Kaitstud magistratöö:

- **K. Kaarna** Growth of $\text{Cu}_2\text{ZnSnSe}_4$ Monograin Powders in Molten Potassium Iodide. *Master Thesis*, Tallinn 2014.

Füüsikaliste mõõtmiste uurimisgrupi teadustöö kirjeldus.
prof. Jüri Krustok

Physical properties of different solar cell materials and solar cells were studied by Raman spectroscopy, photoluminescence spectroscopy, photoreflectance spectroscopy, external quantum efficiency, and electrical measurements. Studied materials were Cu_3BiS_3 , $\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$.

Uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused/The main results:

- The elemental composition, structural, optical and electronic properties of *p*-type Cu_3BiS_3 thin films are investigated. The films are shown to be single phase orthorhombic, with a measured composition of $\text{Cu}_{3.00}\text{Bi}_{0.92}\text{S}_{3.02}$. A surface oxidation layer is also clarified using energy dependent X-ray microanalysis. Photoreflectance spectra demonstrate two band gaps ($E_{gX}=1.24$ eV and $E_{gY}=1.53$ eV at 4 K) associated with the X and Y valence subbands. The photocurrent excitation measurements suggest a direct allowed nature of E_{gX} . Photoluminescence spectra at 5 K reveal two broad emission bands at 0.84 and 0.99 eV quenching with activation energy of 40 meV.
- The influence of the degree of disordering in the cation sublattice on low temperature photoluminescence (PL) properties of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) polycrystals was investigated. Using different cooling rates after post-annealing at elevated temperatures changed the degree of disordering. The results suggest that in the case of higher degree of cation sublattice disorder radiative recombination involving defect clusters dominates at $T = 10$ K. These defect clusters induce local band gap energy decrease in CZTS. Giving more time for establishing ordering in the crystal lattice can reduce the concentration of defect clusters. As a result, radiative recombination mechanism changes and band-to-

impurity recombination involving deep acceptor defect with ionization energy of about 200 meV starts to dominate in the low temperature PL spectra of CZTS polycrystals.

- Temperature dependent photoluminescence (PL) study of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) polycrystals was performed. The low temperature PL spectrum consists of two PL bands: PL1 at 0.66 eV and PL2 at 1.35 eV. We propose a new radiative recombination model involving theoretically predicted $(\text{Cu}_{\text{Zn}}^- + \text{Sn}_{\text{Zn}}^{2+})$ and $(2\text{Cu}_{\text{Zn}}^- + \text{Sn}_{\text{Zn}}^{2+})$ defect clusters in nearly stoichiometric CZTS.

- The band gap of $\text{Cu}_2\text{ZnSnSe}_4$ thin films synthesized by selenization of magnetron sputtered metal precursors was determined from the absorption spectra increases from 1.01 eV at 300 K to 1.05 eV at 4.2 K. In lower quality films photoluminescence spectra show a broad, low intensity asymmetric band associated with a recombination of free electrons and holes localized on acceptors in the presence of spatial potential fluctuations. In high quality material the luminescence band becomes intense and narrow resolving two phonon replicas. Its shifts at changing excitation power suggest donor-acceptor pair recombination mechanisms. The proposed model involving two pairs of donors and acceptors is supported by the evolution of the band intensity and spectral position with temperature. Energy levels of the donors and acceptors are estimated using Arrhenius quenching analysis.

- The optoelectronic and structural properties of $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ (CZTGeSe) alloy compounds with x varying from 0 to 1 with a step of 0.1 were also studied. The crystal structure and the lattice parameters of the CZTGeSe polycrystals were determined by using X-ray diffraction analysis. A linear decrease of the lattice parameter a from 0.569 nm to 0.561 nm with increasing Ge concentration was detected. Raman spectroscopy analysis revealed unimodal behavior and a linear shift of the three A symmetry Raman modes of kesterite crystal structure towards higher wavenumbers with increasing Ge content. Radiative recombination processes in CZTGeSe polycrystals were studied by using low-temperature photoluminescence (PL) spectroscopy. A continuous shift from 0.955 eV to 1.364 eV of the PL band position with increasing Ge concentration was detected. Based on the temperature dependent PL measurements of the CZTGeSe polycrystals, two types of recombination mechanisms were detected: band to impurity recombination in $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ with $x \leq 0.2$, and band to tail recombination in $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$ with $x > 0.2$.

- Temperature dependencies ($T = 10\text{--}300$ K) of current-voltage (J-V) characteristics and external quantum efficiency (EQE) spectra of $\text{Cu}_2\text{ZnSnS}_4$ monograin layer solar cells were measured in order to clarify current transport in CZTS, that is still not fully understood. Three different temperature ranges can be distinguished from the temperature dependence of the series resistance (R_s) obtained from J-V measurements and the effective bandgap energy (E_g^*) determined from the EQE spectra. Thermally activated conductivity, Mott's variable-range hopping conductivity, and very low temperature (< 40 K) blocking of the interface recombination were observed.

Uurimisgrupi olulisemad publikatsioonid aruandeaastal:

1. M. Grossberg, T. Raadik, J. Raudoja, J. Krustok. Photoluminescence study of defect clusters in $\text{Cu}_2\text{ZnSnS}_4$ polycrystals. *Current Applied Physics* 14 (2014) 447-450.
2. M. Grossberg, J. Krustok, T. Raadik, M. Kauk-Kuusik, J. Raudoja. Photoluminescence study of disordering in the cation sublattice of $\text{Cu}_2\text{ZnSnS}_4$. *Current Applied Physics* 14 (2014) 1424-1427.
3. M.V. Yakushev, P. Maiello, T. Raadik, M.J. Shaw, P.R. Edwards, J. Krustok, A.V. Mudryi, I. Forbes, R.W. Martin, Electronic and structural characterisation of Cu_3BiS_3 thin films for the absorber layer of sustainable photovoltaics. *Thin Solid Films* 562 (2014) 195-199.

Õhukeseleliste materjalide uurimisgrupi teadustöö kirjeldus/ prof. Enn Mellikov

The main activities were focused on the synthesis of new attractive material SnS for absorber layers of solar cells. SnS has very high absorption of solar radiation and suitable band gap that allows solar radiation conversion efficiencies up to 30% similar to kesterites. In difference of kesterites, SnS consists of non-toxic and wide-spread elements and is the binary compound that makes easier its use in big production of solar cells.

The aim of the research was to study regularities of chemical bath deposition (CBD) of tin sulphide thin films as function of tin and sulphur concentrations in the solutions. SnS thin films were deposited onto molybdenum (Mo) coated soda lime glass, ITO-coated glass, borosilicate glass and ITO-coated glass substrates at room temperature.

- Development of SnS thin films by chemical bath deposition, electrochemical and vacuum deposition methods, properties of surface morphology, chemical composition and phase composition of the deposited films
- Effect of heat treatments upon the as-deposited SnS thin films occurring in different ambient, such as hydrogen sulfide (H_2S), argon (Ar), and vacuum, at various temperatures and for different durations.
- An additional aim was to develop single-phase SnS photoabsorber layers for the fabrication of solar cells.

Uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused/The main results:

- SnS films have the structure of orthorhombic herzenbergite tin monosulphide with stoichiometric composition and good pin-hole free surface morphology of rod (ZnS substrate) or flake (CdS substrate) shape of the particles. XRD, Raman and EDX analyses didn't show any additional phases in the films. Crystallinity of the as-deposited films improves in multiple deposition process and three times deposited films have well-determined crystalline structure. Grain sizes slightly grow in multiple deposition process of films. Band gap decreases with the thickness of the films and for three times deposited

it is equal to 1.28 eV. Films on both substrates have very high electroresistivity, which should be improved with further chemical and thermal treatments.

- It was additionally shown that phase structure of films depends from the chemical nature of deposition substrate. The additional annealing of obtained SnS films (argon, vacuum, H₂S) improves their phase and crystalline structure and initiates growth of crystals in films. All films deposited onto molybdenum (Mo) coated soda lime glass, ITO-coated glass, borosilicate glass and ITO-coated glass substrates at room temperature for 24 hours had composition of tin monosulphide. The films deposited at concentration of 0.01M had non-uniform and incomplete coverage of the substrate on all used substrates whereas at tin and sulphur concentrations higher than 0.05M films were peeling off the substrate. EDX analyse indicated that these films were tin-rich. SnS films deposited on borosilicate glass were always tin-rich not depending of the used substrate and concentrations of components in deposition solution.
- The microstructural properties of the HVE-SnS thin films influenced by different atmospheres used during annealing. The SnS films annealed in H₂S at 400 °C show changes in the composition from tin monosulfide before annealing to tin disulfide after annealing. The SnS films annealed in an argon atmosphere for 1 h show no significant change in the crystal structure or the compositional uniformity of the film, though degradation of the SnS films occurs after 2 h of annealing at 500 °C. The SnS films annealed in vacuum at 500°C show good crystallinity, dense morphology, and high photosensitivity, and are promising for use as a photoabsorber layer in solar cell structures.

Uurimisgrupi kuni olulisemad publikatsioonid aruandeaastal:

1. Safonova, M.; Nair, P; Mellikov, E.; Garcia, A; Kerm, K.; Revathi, N.; Romann, T; Mikli, V.; Volobujeva, O. (2014). Chemical bath deposition of SnS thin films on ZnS and CdS substrates. *Journal of Material Science: Materials in Electronics*, 25(7), 3160 - 3165.
2. Revathi, N.; Bereznev, S.; Loorits, M.; Raudoja, J.; Lehner, J.; Gurevits, J.; Traksmaa, R.; Mikli, V.; Mellikov, E.; Volobujeva, O. (2014). Annealing effect for SnS thin films prepared by high-vacuum evaporation. *Journal of Vacuum Science & Technology A-Vacuum Surfaces and Films*, 32(6), 061506-1 - 061506-7.

Kaitstud doktoritöö:

Julia Lehner 2014 “Formation of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄ by chalcogenisation of electrochemically deposited precursor layers” (juhendajad E. Mellikov, O. Volobujeva)

Mobiltas järeldoktor **Naidu Revathi** 01.02.12 – 31.01.15 (juhendaja Olga Volobujeva)

2.2 Keemiliste kiletehnoloogiate teaduslaboratoorium, Laboratory of Thin Film Chemical Technologies, juhataja M. Krunk

Teadustöö kirjeldus/ Description of the research

Studies have been performed in the next research areas:

- Deposition of metal oxide (ZnO, p-NiO) thin films and ZnS nanorod layers by chemical spray and ZnO nanorod layers by electrochemical deposition techniques, properties of nanostructured layers
- Preparation and properties of plasmonic materials, properties of Au nanoparticles doped absorber layers, use of plasmonic absorbers in solar cells
- Deposition of Earth abundant Sn_xS_y absorber layer by chemical spray method, properties of thin films
- Development of chemical bath deposited CdS and close space sublimated CdTe films for efficient solar cells, characterization of thin films and use in solar cells

Tähtsamad teadustulemused/ Main scientific results

- It was shown for the first time the possibility to grow not only ZnO nanorods but also ZnS nanorod arrays by non-vacuum technique of chemical spray in air. We studied the effect of molar ratio of Zn and S precursors in the spray solution and growth temperature on the phase composition, morphology and optical properties of ZnS layers. Main factor determining the purity of sulfide phase is amount of thiourea in the solution sprayed as only with excess of sulfur source pure ZnS phase is obtained. Development of ZnS nanorods is controlled by both the phase purity and growth temperature.
- It was important to find new possible application fields for nanostructured layers fabricated by solution techniques and for this reason we studied photocatalytic properties of different nanostructured layers. It appears that ZnO nanostructured layers have excellent photocatalytic activity which could be efficiently used to clean waste waters from organic pollutants.
- The methodology to grow ZnO layers on light flexible polymeric substrates as substrates for next-generation light solar cells or transparent electronic devices was elaborated. It was shown that an un-doped ZnO should be deposited first which acts as a seed layer for the following n-ZnO layer (ZnO:In). It was shown that depend on the seed layer morphology flat compact film or scrolled nanobelts of ZnO:In could be grown. The layer morphology determines the electrical properties such as carrier mobility and electrical resistivity, while the carrier concentration is mainly determined by the amount of donor states in the material.
- Metal oxide films with p-type of conductivity are of high importance in electronic devices and also in solar cells. P-NiO films were grown by chemical spray using two different precursor materials. Smooth films were obtained with Ni acetate while rough and porous films formed from Ni chloride. Doping with Li ions of NiO films grown from acetate was used to adjust the concentration of holes in NiO film.
- In 2014, main focus has been set to the development of plasmonic materials. The technologies to prepare Plasmonic nanoparticles of Au and Ag by techniques of sol gel

and spray have been elaborated. Thermoanalytical studies of precursors for Au and Ag nanoparticles provide with data to select nanoparticle deposition temperatures. Methodology of applying noble metal nanoparticles into or onto the films was worked out on TiO₂ films as an inactive model material. Application of Au nanoparticles into the CuInS₂ and CdTe absorber layers results in an additional absorption band at 600-800 nm in the optical spectrum of the absorber layer, caused by surface plasmon resonance effect of Au nanoparticles in absorber. The band width and intensity is controlled by the amount, size and distribution of Au particles in an absorber layer. Use of CuInS₂+Au nanoparticles layer in thin film solar cells increases the conversion efficiency as enhanced light absorption has increased the photocurrent density.

In this field we published 8 full research papers in 2014. Experiments with plasmonic CdTe absorber solar cells were also successful and the research article is submitted for publication.

- We studied deposition and properties of metal sulfide films such as In₂S₃ (prospective absorber for intermediate absorber solar cell) and Sn_xS_y (potential absorber for thin film solar cell) grown by non-vacuum chemical spray pyrolysis method. According to Raman spectroscopy study the crystal quality of In₂S₃ increases when deposited at higher temperatures or with an alcohol solvent or applying post-deposition thermal treatment in diluted H₂S atmosphere. Simultaneously, an increase in quality of crystal ordering with Indium in octahedral sites was observed. Earth abundant Sn_xS_y films with reduced content of oxidated phases can be grown by spray using thiourea-rich spray solutions.

- In the field of development of materials for more efficient CdS/CdTe solar cells we have identified formation regularities of the structural properties of CdTe thin films deposited by close spaced sublimation in dependence on the temperature of the substrate and got understanding of the impact of oxychloride activation treatment on the optoelectronic properties of these thin films. Investigations on impact of annealing in different atmospheres on structural, optical and electrical properties of chemical bath deposited CdS thin films revealed that the induced by annealing changes in the properties are connected with decomposition of OH⁻ group incorporated in CdS lattice in the deposition process, with outdiffusion of H₂O and destruction of crystallites, and with creation of Cd excess resulting in transition from CdS_{1-x}(OH)_x to CdS_{1-y}O_y solid solution. Annealing in air and N₂ creates stable CdS_{1-y}O_y solid solution while H₂ annealing removes the oxides and chloride dopant resulting in pure CdS films. Excess of Cd as precipitate decreases the transmittance while incorporation of oxygen into CdS lattice decreases the band gap of the CdS film. As a result of these studies, application of layers with improved properties allows increase efficiencies of CdS/CdTe by 2%, i.e. to 12% for the best cells.

2014. aastal avaldati 23 teadusartiklit, sh 20 ISI artiklit ja 3 konverentsikogumiku artiklit, kaitsti 1 doktoritöö. 23-st avaldatud publikatsioonist on 20 artiklit otseselt meie labori teematikas, 3-s artiklis olime kaasatud kaasautoritena.

5 olulisemat publikatsiooni:

1. I.Oja Acik, L. Dolgov, M. Krunks, A. Mere, V. Mikli, S. Pikker, A.Loot, I.Sildos, Surface plasmon resonance caused by gold nanoparticles formed on sprayed TiO₂ films, *Thin Solid Films*, 2014, 553, 144-147
2. A. Katerski, E. Kärber, I. Oja Acik, L. Dolgov, A. Mere, I. Sildos, V. Mikli, M. Krunks. Modification of light absorption in thin CuInS₂ films by sprayed Au nanoparticles, *Nanoscale Research Letters*, 2014:9494
3. T. Dedova, M. Krunks, I. Gromyko, V. Mikli, I. Sildos, K. Utt, T.Unt, ZnS thin films and ZnS nanorods by spray pyrolysis: Effect of growth temperature and Zn:S molar ratio in solution on properties of ZnS layers. *Physica Status Solidi A*, 2014, 211 (2) 514-521.
4. E. Kärber, A. Katerski, I. Oja Acik, V. Mikli, A. Mere, I. Sildos, M.Krunks. Low-cost plasmonic solar cells by chemical spray pyrolysis method. *Beilstein J. Nanotechnology*, 2014, 5, 2398-2402
5. K. Otto, I. Oja Acik, M. Krunks, K. Tönsuaadu, A. Mere. Thermal decomposition study of H₂AuCl₄·3H₂O and AgNO₃ as precursors for plasmonic metal nanoparticles. *J. Therm. Anal. Calor.*, 2014, 118, 1065-1072

Kaitstud doktoritööd:

Erki Kärber 2014 “Properties of ZnO-nanorod/In₂S₃/CuInS₂ Solar Cell and the Constituent Layers Deposited by Chemical Spray Method” (Juh. M. Krunks, A.Mere)

Kaitstud magistritööd:

Gboyega Nathaniel Oyekoya 2014 “Chemical spray deposition of Au-nanoparticles and TiO₂:Au film” (Juh. I.Oja Acik, A. Katerski)

Inga Gromõko 2014 “ZnO nanostruktureeritud kihid keemilistel vedelik sadestusmeetoditel” (Juh. T. Dedova, M. Krunks)

US patent US 8,808,801 B2, välja antud: Aug.19, 2014

Autorid: **Malle Krunks, Ilona Oja Acik, Tatjana Dedova**

Pealkiri: Method of preparing ZincOxide nanorods on a substrate by chemical spray pyrolysis

2.3 Füüsikalise keemia õppetool, Chair of Physical Chemistry, prof. Andres Öpik

Molekulaarselt jäljendatud polümeeride uurimisgrupi teadustöö kirjeldus (inglise keeles)/ V. Syritski, A. Öpik

The Molecularly Imprinted Polymers (MIP) group at the Department of Materials Science is involved in projects addressing at development of robust label-free recognition elements for chemical sensing based on Molecularly Imprinted Polymers. The research activities are focused mainly on (i) careful optimization of the MIP films preparation strategy and (ii) study of target analyte re-binding on the MIP-modified sensors.

The optimization of MIP films preparation strategy includes the following:

- computational simulations of the molecular interactions between different functional monomers and template-target molecules (IgG, antibiotics);
- sensor surface functionalization by electrodeposition of different *p*-substituted benzene diazonium layers for the subsequent biomolecule immobilization;
- use of different polymer matrices and electrochemical synthesis conditions to prepare MIP films on sensor surfaces;
- careful control of the polymer film thickness during the electrodeposition process;
- finding optimal procedure for the template (IgG, antibiotics) removal from the polymer matrix;
- enhancement of recognition capacity of antibiotic-MIP films modifying preliminary sensor surfaces by different dextran (Dex) layers;
- development of a strategy for MIP films preparation using living radical photopolymerization technique.

The study of analyte re-binding on MIP-modified sensors includes the following:

- use of different label-free detection techniques such as Surface plasmon resonance (SPR), Quartz crystal microbalance (QCM) and Surface acoustic wave (SAW);
- study of the possibility to block the non-specific rebinding of analyte on IgG-MIP-modified SAW chip using the injections of HSA at different concentrations;
- study of the selectivity of the IgG-MIP-modified SAW chip with respect to IgA and HSA;
- study of the selectivity of antibiotic-MIP-modified QCM or SAW sensors in the presence of interfering compounds.

Tähtsamad teadustulemused/ Main scientific results

- Computational simulations revealed high probability of the formation of hydrogen bonding between *m*-phenylenediamine (mPD) and antibiotic, sulfamethizole (SMZ), as well as multiple hydrogen bonding between mPD and IgG molecule;
- Maleimide benzene diazonium electrochemical reduction provided a reliable surface functionalization method for subsequent biomolecule immobilization;
- Poly(*m*-phenylenediamine) (PmPD) was found to be suitable for polymer matrix formation in term of showing the lowest “non-specific” binding among different

polymers tested (polypyrrole, poly(3,4-ethylenedioxythiophene), polydopamine) and producing a homogeneous and uniform polymer film during electropolymerization on the IgG-modified sensor surface as well as in the presence of antibiotics.

- The optimal polymer thickness for IgG-MIP films was found to be 10.6 nm and for SMZ-MIP films 30 nm.
- The optimal IgG removal procedure was developed considering the specificity of the IgG-MIP preparation strategy such as the use of cleavable linker for IgG immobilization as well as the possibility of the multiple non-covalent interactions between antibody and polymer matrix.
- The method for photoinitiator attachment to the sensor surface was developed. The influence of UV-illumination time on the thickness of photopolymerized poly(2-(diethylamino)ethyl methacrylate) films was studied.
- The SMZ-MIP(Dex) films prepared on the Dex-modified QCM sensor surface demonstrated higher specific recognition capacity compared with SMZ-MIP films.
- It was demonstrated that IgG-MIP and SMZ-MIP integrated with SAW chips were capable to detect analyte, IgG and SMZ, respectively, in lower concentration compared to QCM and SPR sensing platforms.

Uurimisgrupi olulisemad publikatsioonid aruandeaastal:

1. Zhang, X.; Rosicke, F.; Syritski, V.; Sun, G.; Reut, J.; Hinrichs, K.; Janietz, S.; Rappich, J. (2014). Influence of the Para-Substituent of Benzene Diazonium Salts and the Solvent on the Film Growth During Electrochemical Reduction. *Zeitschrift Fur Physikalische Chemie-international Journal of Research in Physical Chemistry & Chemical Physics*, 228(4-5), 557 - 573.
2. Kanyong, P.; Sun, G.; Rösicke, F.; Syritski, V.; Panne, U.; Hinrichs, K.; Rappich, J. (2015). Maleimide functionalized silicon surfaces for biosensing investigated by in-situ IRSE and EQCM. *Electrochemistry Communications*, 51, 103 - 107.

A2B6 materjalide uurimine / K. Lott

The scientific reason for this is also the fact that solid-state chemistry of II-VI materials has come of age in the past few years because of the opportunity of creation of *p*- and *n*-type crystals of these compounds using co-doping processes.

Our present method for investigation concerns the relationships between point defect equilibria and their properties. Point defect equilibria depend on the temperature *T*, the component vapour pressure *P*, and on the chemical potentials of components μ_k . These parameters determine the concentration of defects and native point defect concentration isotherms and isobars were under experimental investigation.

High temperature electrical conductivity (HTEC) in undoped hydrothermally grown ZnO single crystal is investigated. HTEC measurements were performed under the Zn component vapor pressure (up to 1 atm) and in the temperature range from 873 K to 1273 K. Reliable thermodynamic equilibrium in the ZnO crystal for HTEC measurements

of isotherms and isobars was obtained at the temperatures higher than 873 K. Surprisingly slow chemical diffusion prolonged the high temperature measurement cycles continuously for several weeks. In our experiments the absolute value of HTEC in undoped hydrothermally grown ZnO was several orders of magnitude higher than HTEC in undoped ZnS. Slopes of HTEC isotherms varied with component vapor pressure and changed in the range from 0.2 to 0.4. For HTEC isobar in the temperature range from 1173 K to 1273 K it was found activation energy value 0.3-0.4 eV at zinc vapour pressure 0.092 atm.

Uurimisgrupi olulisem publikatsioon aruandeaastal:

1. K. Lott, T. Nirk, L. Türn, A. Öpik, E. Kortunova, P. Shvanskiy, E. Gorokhova, and A. Vishnjakov, *Phys. Stat. Sol. (c)* 11, 1481 (2014)

3. Loetelu struktuuriüksuse töötajate rahvusvahelistest tunnustustest.

Rahvusvahelised tunnustuse 2014 a. puuduvad

4. Loetelu struktuuriüksuse töötajatest, kes on välisakadeemiade või muude oluliste T&A- ga seotud välisorganisatsioonide liikmed.

Enn Mellikov	EV esindaja EL koostöövõrgus MEERA, EERA-PV
Maarja Grossberg	esindaja koostöövõrgus EERA-PV, PV-Baltic
Dieter Meissner	esindaja koostöövõrgus PV-Baltic
Marit Kauk-Kuusik	esindaja koostöövõrgus Nordic-PV
Olga Volobujeva	esindaja koostöövõrgus PV-Baltic, teaduskomitee liige MEERA-s

5. Soovi korral esitatakse aruandeaastal saadud T&A-ga seotud tunnustused, ülevaade teaduskorralduslikust tegevusest, teadlasmobiilsusest ning hinnang oma teadustulemustele.

Tunnustused 2014:

- **Inga Gromõko** - Eesti üliõpilaste teadustööde konkursil loodusteaduste ja tehnika valdkonnas magistriõppe üliõpilaste astmes 1. Preemia
- **Inga Gromõko** – parim posterettekanne FMNT 2014 konverentsil Riias, 28.sept.-2.okt. 2014.
- **Malle Krunk** – TTÜ aasta teadlane

2014. aastat võib pidada Materjaliteaduse instituudile edukaks. Instituudi teadustegevuse tulemuslikkusest annab tunnistust 50 publikatsiooni rahvusvahelistes retsenseeritud väljaannetes, samuti ligi 60 esinemist rahvusvahelistel seminaridel ja konverentsidel.

Teadustöö on olnud koordineeritud 2014 aastal 2 EV tippkeskuse projekti, 6 EV riikliku programmi, 2 PUT-i, 2 IUT-iga, lisaks 7 Teadusfondi granti, siseriiklikud ja välislepingud

ning Euroopa 7. RP projekt ning baasfinatseerimise lepingud. Projektides osalevad väga aktiivselt ja tulemuslikult ka doktorandid, magistrandid.

Aktiivne on olnud ka teaduskorralduslik tegevus. Esile võib tõsta Materjaliteaduse instituudi poolt korraldatud rahvusvahelist töötuba "5th European Kesterite Workshop", mis toimus 13-14. novembril 2014 Tallinna Tehnikaülikoolis Materjaliteaduse insituudi eestvedamisel järjekorras juba viiendat korda. Sellel üritusel osales 80 teadlast 13 riigist üle Euroopa ja ka Austriaaliast.

Euroopa Kesteriitide Töötoa loomise ajendiks oli vajadus tugevdada rahvusvahelist koostööd kesteriitsete absorbermaterjalidega tegelevate uurimisgruppide vahel, et luua alus Eesti Vabariigi teadlaste edu jätkumisele antud teadustemaatikas ja ühistele rahvusvahelistele projektidele ning koostööle. Antud töötuba on väga oluline, et suurendada EV teaduse rahvusvahelist nähtavust, atraktiivsust ja konkurentsivõimet, et edendada meie vabariigis teadusuuringuid, mille põhieesmärgiks on uurida ja arendada uusi materjale päikeseenergeetikale nagu seda on kesteriitsed absorbermaterjalid. Töötoa toimumine Tallinnas andis võimaluse veelgi parandada Eesti Vabariigi tehnikateaduste rahvusvahelist nähtavust.

Samuti tuleb ära märkida prof. A. Öpiku osalus "Baltic Polymer Symposium 2014" korralduskomitees. Selles üritusest võttis osa üle 130 teadlase ja tudengi 15 erinevast riigist.

Pooljuhtmaterjalide õppetooli teaduslike tulemustega on otseselt seotud arendustööd firmaga crystalsol OÜ.

MTI kuulub jätkuvalt mitmetesse rahvusvahelistesse teaduskoostöö võrkudesse PV ja materjalide valdkondades: M-ERA, EERA-PV, PV-Baltic ja EUKENE (European Kesterite Network).

Materjaliteaduse instituudi nõukogu hinnang 2014 a. T&A tegevusele on väga hea.

Teadusosakond koostab lootelud struktuuriüksuses aruandeaastal täidetavate projektide (Eesti Teadusinfosüsteemi, edaspidi ETIS, andmetel), avaldatud kõrgetasemeliste eelretsenseeritud publikatsioonide, kaitstud doktoriväitekirjade, järel doktorina T&A-s osalenud isikute, loodud tööstusomandi ja taristu uuendamise kohta ning avaldab need TTÜ teadus- ja arendustegevuse vastava aasta koondaruande lisana.