MATEMAATIKA-LOODUSTEADUSKOND
FÜÜSIKAINSTITUUT
TEADUS- JA ARENDUSTEGEVUSE AASTAARUANNE 2014

1. Struktuur

Füüsikainstituut, Department of Physics
Instituudi direktor Pavel Suurvarik

- Rakendusfüüsika õppetool, Chair of Applied Physics, Jüri Krustok
- Teoreetilise füüsika õppetool, Chair of Theoretical Physics, Rein-Karl Loide

2. Teadus- ja arendustegevuse (edaspidi T&A) iseloomustus

2.1 Struktuuriüksusesse kuuluvad uurimisgrupid *(kõik uurimisgrupid näidatakse aruandes eraldi, järgides alltoodud ülesehitust).*

Uurimisgrupi nimetus *(eesti ja inglise keeles)* **ja juhi nimi**

- uurimisgrupi teadustöö kirjeldus *(inglise keeles*);
- uurimisgrupi aruandeaastal saadud tähtsamad teadustulemused *(inglise keeles);*
- uurimisgrupi kuni 5 olulisemat publikatsiooni aruandeaastal.

- **Chair of Applied Physics , 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, Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ and $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$.

  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 $Cu_{3.00}Bi_{0.92}S_{3.02}$. 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 sub-bands. 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 an activation energy of 40 meV.

  We also investigated the influence of the degree of disordering in the cation sublattice on low temperature photoluminescence (PL) properties of Cu_2ZnSnS_4 (CZTS) polycrystals. The degree of disordering was changed by using different cooling rates after post-annealing at elevated temperatures. 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. The concentration of defect clusters can be reduced by giving more time for establishing ordering in the crystal lattice. 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 Cu_2ZnSnS_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 $(Cu_{Zn}^{-} + Sn_{Zn}^{2+})$ and $(2Cu_{Zn}^{-} + Sn_{Zn}^{2+})$ defect clusters in nearly stoichiometric CZTS.

In the next study $Cu_2ZnSnSe_4$ thin films were synthesised by selenisation of magnetron sputtered metal precursors. The band gap 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 localised 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 $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ (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 $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ with $x \leq 0.2$, and band to tail recombination in $Cu_2Zn(Sn_{1-x}Ge_x)Se_4$ with $x > 0.2$.

In the next study temperature dependencies (T = 10–300 K) of current–voltage (J–V) characteristics and external quantum efficiency (EQE) spectra of Cu_2ZnSnS_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.

Parimad tööd:

- M. Grossberg, T. Raadik, J. Raudoja, J. Krustok. Photoluminescence study of defect clusters in Cu_2ZnSnS_4 polycrystals. Current Applied Physics 14 (2014) 447-450.
- M. Grossberg, J. Krustok, T. Raadik, M. Kauk-Kuusik, J. Raudoja. Photoluminescence study of disordering in the cation sublattice of Cu2ZnSnS4. Current Applied Physics 14 (2014) 1424-1427.
- Yakushev, M.V.; Maiello, P; Raadik, T; Shaw, M.J.; Edwards, P.R.; Krustok, J.; Mudryi, A.V.; Forbes, I.; Martin, R.W. Electronic and structural characterisation of Cu_3BiS_3 thin films for the absorber layer of sustainable photovoltaics. Thin Solid Films 562 (2014) 195-199.

Chair of Theoretical Physics, Rein-Karl Loide (kuni 31.08.2014)

– The main reseach topics are related to molecular dynamics (MD) simulations of the nanomaterials (nanotubes, graphene) and studied the physical properties of alkaline-earth metals hydroxides by density functional theory (DFT) method. The studies were performed in collaboration with the Institute of Physics of the Tartu University and Department for Solar Energy of the Institute for Energy Technology (Norway).

Main results:

The two types of conjoined structures of carbon nanotubes (CNT) and nanoribbons (NR): 1)caused by van der Waals forces with the approximate distance 0.34 nm between CNT and the NR and 2) with the chemical bonds of the length 0.16 nm acting between the nearest C6 rings of CNT andGNR. The first structures, if the length of CNT is smaller than the width of GNR, constitute the CNTs attached to GNRs bent on a finite angle. These structures may allow one to obtain a low-density material consisting of the mixture of short CNTs and somewhat broader NRs. If CNT had the same or larger length than the width of NR and it was initially situated at the end of the NR, the nanotube was found to be revolving upon the NR. In this way one can obtain the nanotubes-like lengthy scrolls of GNRs of an arbitrary thickness. These multi-wall CNT-type nanoscrolls should have unique mechanical properties together with possibly useful electrical properties. The second-type structures are metastable. However, they also may be of practical importance due to larger mechanical strengths and new electrical properties. The calculations of carbon structures performed by us show also the existence of a new 3D metastable carbon allotrope consisting of chemically bounded graphene sheets with the interplane distance 0.16 nm and with the hollow configuration of conjoined C6 rings. This hypothetical material can be called as volumetric graphene. Performed the DFT calculation of the fundamental electronic properties of a wide-gap CaSO4 crystal doped with Gd3+ , Dy3+ , Tm3+ , and Tb3+ ions in a spectral region connected with the electron transitions from narrow outermost p-subbands of the valence band to s- and d-subbands of the conduction band. The experimental manifestations of the theoretically predicted self-trapping of p-holes have been revealed. At T > 35 K, a hopping diffusion of heavy hole polarons toward the electrons localized at/near RE3+ impurity ions with an initial odd number of 4f electrons takes place resulting in the excitation of a typical emission of 157 Gd3+ , Dy3+ , or Tm3+ impurity centres.

The existing of moving ILMs (with energy around 1 eV) in metals Cu, Fe and Ni (EAM potential) and high localized ILMs in solicon (tersoff potential) and diamond (lcbop potential) over the phonon spectrum was shown by molecular dynamics simulations. By hybrid pseudopotentials method calculated the real band gap in magnesium and calcium hydroxides. Shown the existing of localized (high-energy) excitons and calculated the optical spectrums in these materials.

Parimad tööd:

- Krasnenko, V; Boltrushko, V.; Klopov, M.; Hizhnyakov, V. (2014). Conjoined structures of carbon nanotubes and graphene nanoribbons. Physica Scripta, 89(4), 044008
- Kudryavtseva, I; Klopov, M; Lushchik, A; Lushchik, Ch; Maaroos, A; Pishtshev, A. (2014). Electronic excitations and self-trapping of electrons and holes in CaSO4. Physica Scripta, 89(4), 044013
- Pishtshev, A.; Karazhanov, S. Zh.; Klopov, M. (2014). Excitons in Mg(OH)2 and Ca(OH)2 from ab initio calculations. Solid State Communications, 193, 11 - 15.
- Pishtshev, A.; Karazhanov, S. Zh.; Klopov, M. (2014). Materials properties of magnesium and calcium hydroxides from first-principles calculations. Computational Materials Science, 95, 693 - 705.
- Hizhnyakov, V.; Haas, M.; Shelkan, A.; Klopov, M. (2014). Theory and molecular dynamics simulations of intrinsic localized modes and defect formation in solids. Physica Scripta, 89(4), nr 044003

– Photogrammetrical study of lunar surface photographs made by the crew of Apollo 12 during their 2 extravehicular activities (EVA). The camera stations map was created and appended, it contains locations and attitude angles of 298 individual cameras. Locations and orientations of Surveyor 3 lunar probe and all ALSEP instruments were found, accuracy estimations were made. The results are being prepared for publication.

Main results:

Results of the previous photogrammetrical study of Apollo 11 landing site have been accepted for publication in Journal of the British Interplanetary Society (JBIS). Results of algebraic analysis of Sriyantra studied were published by Indian Journal of History of Science (IJHS).

Parimad tööd:

- V-V. Pustynski, E. M. Jones, Photogrammetry of Apollo 11 Surface Imagery. Journal of the British Interplanetary Society (in press).
- V-V. Pustynski. On Mathematical Complexity of Sriyantra. Indian Journal of History of Science, volume 9, issue 3, September 2014.

– Quantum field theory.The studies of relativistic wave equations for arbitrary spin (superspin) fields and superfields, algebras and superalgebras are continued.

Main results:

Superfield equations of motion in the case of massive and massless fields are presented together with an application in linear supergravity.

We have developed an interesting approach to fields and superfields of arbitrary spin and superspin.

Parimad tööd:

- Loide, R.-K., Suurvarik, P. (2014). Supersymmetry: superfield equations of motion. Journal of Physics: Conference Series (012016-1 - 012016-7).Institute of Physics Publishing

2.2 Loetelu struktuuriüksuse töötajate rahvusvahelistest tunnustustest.

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

2.4 Soovi korral esitatakse aruandeaastal saadud T&A-ga seotud tunnustused (va punktis 2.3 toodud tunnustused), ülevaade teaduskorralduslikust tegevusest, teadlasmobiilsusest ning hinnang oma teadustulemustele.