THIN FILM LAYERS AND MULTILAYER NANOSTRUCTURES FOR PHOTOVOLTAIC APPLICATIONS

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Joint Institute of Solid State and Semiconductor Physics of the National Academy of Sciences of Belarus (JISSSP NASB)

- JISSSP was established in 1963.
- At present, the Institute is a leader in the field of the solid state and material science in Belarus. JISSSP is carrying out investigations in the field of single crystals, thin films, amorphous and microcrystalline materials, composites, powders and methods for their compaction and radiation effects on solids.
- JISSSP staff: about 164 research fellows, among them 1 academician, 2 Corresponding Members of Belarus Academy of Sciences, 13 Full-Doctors of Science and 83 PhDs working in 14 laboratories and 3 manufacturing enterprises.
Basic fields of research

The Institute is carrying out basic investigations in various fields of the solid state physics: solid state theory, physics of magnetism and ferroelectricity, semiconductor physics, high-temperature superconductors and highly pure metals in special conditions, superhard materials, crystal growth, radiation effects on solids, interaction of optical emission with condensed matter. The Institute also carries out applied research in frames of the above mentioned research fields.

Promising studies into new materials

1) Thin films produced by various methods
2) High-temperature superconducting materials
3) Amorphous and nanocrystalline alloys
4) Composite materials
5) Semiconducting materials
6) Growing of single crystals and sintering of ceramic samples at temperatures up to 1600 °C
## Experimental methods for investigations of crystals and thin films

### Optical methods

<table>
<thead>
<tr>
<th>Method</th>
<th>Details</th>
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<tbody>
<tr>
<td>Photoluminescence</td>
<td>- wide spectral region 0.2 – 3.5 µm, temperature of measurements 4.2 - 300 K</td>
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<tr>
<td>Photoluminescence excitation</td>
<td></td>
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<tr>
<td>Transmission</td>
<td>- spectral region 50 – 6000 cm⁻¹</td>
</tr>
<tr>
<td>Reflection</td>
<td>- magnetic field up to 10T at 4.2K</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td></td>
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<tr>
<td>Magneto-optical measurements</td>
<td>- un axial stress up to 1 GPa</td>
</tr>
<tr>
<td>Piezo-optical measurements</td>
<td>splitting and shifting of narrow lines in optical spectra (bound and free excitons in semiconductors)</td>
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</tbody>
</table>

### Electrical methods

<table>
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<th>Method</th>
<th>Details</th>
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<tbody>
<tr>
<td>Hall effect</td>
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<tr>
<td>Van-der-Pauw</td>
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<td>Deep Level Transient Spectroscopy</td>
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### Structural method and chemical analysis

<table>
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<th>Method</th>
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<td>X-ray diffraction (XRD)</td>
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<tr>
<td>Energy dispersive X-ray microprobe analysis (EDX)</td>
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<tr>
<td>Scanning Electron Microscopy (SEM)</td>
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<tr>
<td>Auger Electron Spectroscopy (AES)</td>
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Outline

• Introduction
• Preparation of In$_2$S$_3$ thin films
• Structural, chemical composition and optical properties of films
• Characterization of Cu(In,Ga)Se$_2$ thin film solar cells
• Conclusions
In most laboratories, the standard device structure of Cu(In,Ga)Se$_2$ (CIGS)-based solar cells includes a very thin chemical-bath-deposited (CBD) CdS buffer layer between the CIGS absorber layer and the transparent ZnO front electrode. The beneficial effects of the buffer layer range from modifying the CIGS surface chemistry to protecting the sensitive interface during the subsequent window deposition. Peak efficiencies of 19.9% were demonstrated on 0.5 cm$^2$ laboratory cells and 13% on 60×120 cm$^2$ modules. In the last decade, serious efforts to substitute the CdS buffer layer by other nontoxic low absorbing materials have been made for the following reasons:

(a) The expected environmental risks arising from implementation of a CBD CdS process in a CIGS module production line. Cadmium is a toxic heavy metal and can cause at least reputational problems.

(b) The expected technological problems caused by a no vacuum CBD process in a vacuum line.

(c) The potential of increasing current generation in the spectral region of 350–550 nm, and therefore increasing the cell efficiency.

(d) The prohibition of cadmium in electrical or electronic equipment by legal regulations in different countries which can be a marketing problem for Cd-containing CIGS-based thin-film modules.
Crystals of In$_2$S$_3$ binary compound (target material) were grown by directional crystallization of the melt (horizontal variant of the Bridgman method). The ampoule in this method is placed in a two-zone horizontal furnace, temperature of the zones can be controlled independently each other, so that indium and sulfur are placed in different parts of the ampoule.

Deposition of In$_2$S$_3$ films was carried out in the vacuum evaporation installation at residual gas pressure not worse than $5 \cdot 10^{-4}$ Pa. The quartz wafers served as a substrates. The distance between the evaporator and a substrate is 20 cm.

1- water cooled electric contacts;
2 - heater;
3- support;
4- substrate holder;
5- heater;
6 – substrate;
7- In$_2$S$_3$ ;
8-clamp;
9- thermocouple.
### Experimental technique for the investigation of $\text{In}_2\text{S}_3$ films

<table>
<thead>
<tr>
<th>Property</th>
<th>Technique</th>
<th>Instrument/Equipment</th>
</tr>
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<tbody>
<tr>
<td>Surface morphology</td>
<td>Scanning electron microscopy</td>
<td>JEOL 6400 SEM</td>
</tr>
<tr>
<td>Microstructure</td>
<td>Atomic forces microscopy</td>
<td>NT-206 scanning force microscope</td>
</tr>
<tr>
<td>Chemical composition</td>
<td>Dispersive X-ray Auger electron spectroscopy</td>
<td>CAMECA SX-100 Perkin Elmer Physics Electronic 590</td>
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<td>The depth profiling</td>
<td>X-ray diffraction</td>
<td>Siemens D-5000</td>
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<td>Crystalline structure</td>
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<td>Carry 500 Scan UV-Vis-NIR spectrophotometer</td>
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<tr>
<td>Transmission and reflection</td>
<td>Spectral range 200-3000 nm</td>
<td></td>
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<tr>
<td>Measurements</td>
<td>Temperature 300K</td>
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</table>
SEM and XRD patterns of \( \text{In}_2\text{S}_3 \) films

Indium sulfide films have been thermally deposited with average velocity 0.5 nm/s at temperatures \( T_s = 220-240 \, ^\circ\text{C} \).

The XRD spectra of all samples exhibited a broad hump in the 2θ range of around 20º–40º, and this indicated that the all samples deposited at slightly various but relatively low temperatures are amorphous in nature. Our result of amorphous nature of the indium sulfide films thermally deposited at \( T_s = 220-240 \, ^\circ\text{C} \) is consistent with the literature report.
The AES analysis showed that the film becomes slightly rich in indium starting from half of thickness of the film. Although near substrate regions of the sample exhibited a S/In ratio of about 1, which is sulfur deficient, it is also certain that standard $\text{In}_2\text{S}_3$ composition ratio are detected near the film surface. This could be due to the presence of more than one phases in the films. Hence it can be predicted that the oxygen in the films is not only the surface oxidation, but presents as an impurity element. Also, certain ratio of the indium is expected to be present in the form of $\text{In}_2\text{O}_3$ and/or $\text{In(OH)}_x$ (which cannot be determined by the AES technique).
The optical characteristics of the film samples of various thickness are summarized in Fig. All investigated films of different $h$ are characterized by high transmittance ($T \sim 85\%$) in the long wavelength region (500–3000 nm) and a clear absorption edge position. The energy $E_g$ corresponding to the optical absorption edge for the selected film samples with the thickness 800, 300, 120, and 50 nm varies in the range from 1.96 to 3.6 eV.
Optical spectra (a) and morphology (b) of indium sulfide film sample thermally deposited with thickness \( h \approx 800 \) nm. We have discovered that the high concentration of granules of bigger size \( d_1 \) are characteristic for films with thickness \( h > 450 \) nm. The position of band edge of the films is effected mainly by the phase related bigger granules and estimated to be \( E_g = 1.96 \) eV.
Optical spectra (a) and morphology (b) of indium sulfide film sample thermally deposited with thickness $h \sim 300$ nm.

The decrease of the film thickness up to $h = 300–250$ nm results in a significant reduction of bigger granules content and in an increase of middle-size granules concentration. The evidence of two components in the film band edge absorption is attributed to increase of the contribution of middle-size granules. The value of $E_g$ for In$_2$S$_3$ thin films with thickness $h \sim 300$ nm was determined to be about 2.3–2.35 eV.
Optical spectra (a) and morphology (b) of indium sulfide film sample thermally deposited with thickness $h \sim 170$ nm. Film samples with $h = 200–120$ nm have higher concentration of 30–60-nm granules and so we can discard the quantum size effects. It is possible that our films contain some amount of oxygen, however in our case, the bigger In$_2$S$_3$ granules exhibited long-wave shifted $E_g$, while the middle-sized In$_2$S$_3$ granules showed $E_g \sim 2.3–2.35$ eV.
Optical spectra (a) and morphology (b) of indium sulfide film sample thermally deposited with thickness $h \sim 35$ nm. We detected that the thinner films were mainly composed of small particles (1–2 nm). The related band edge position is found to be $E_g = 3.45-3.6$ eV. This result can be explained by the oxygen, quantum size and the amorphous state effects take place in the former particles.
Sequence of steps of CIGS solar cells manufacturing

1. Cleaning of substrates
2. DC magnetron evaporation of Mo
3. Evaporation of Cu, In, Ga precursors (thermal, ion-beam, e-beam)
4. Selenization in Se vapour
5. Films quality control
6. CBD of CdS buffer layer or In$_2$S$_3$ evaporation
7. DC magnetron deposition of i-ZnO
8. DC magnetron deposition of ZnO·Al
9. Ni-Al grid mask patterning
10. Mechanical scribing of samples
11. PV test


**FORMATION OF Cu(In,Ga)Se$_2$ FILMS**

“Method for preparation of Cu(In,Ga)Se$_2$ solid solution films”

Russian Patent No 2236065. Priority 20/05/2003

The temperature and time during process varied in order to optimize the material properties of the CIGS films.

**Stage 1** - Selenium inclusion into the precursor and formation of binary phases at 250 °C.

**Stage 2** - Formation of the CIGS thin films at 250 - 520 °C. No significant improvements in the film structure properties was noticed with a further increase in temperature.
Studies of the static current-voltage characteristics showed that the obtained structures exhibit pronounced rectification. The initial portion of the I-V characteristic (U<0.5 V) for these structures is consistent with well-known diode equation. The value of β indicates that the current is caused by recombination of charge carriers in the active region of these solar cells. The reverse portion of the I-U characteristics are typically described by the power-law dependence |I| ~ |U|^m, where m is found to be close to unity at |U| ≤ 0.3 V, which may indicate that there is tunneling of charge carriers or limitation of the current by the space charge in the saturation mode. At the reverse-bias voltage (|U| > 0.4 V), the value of m = 1.6 and typically related to the currents limited by the space charge for the ballistic mode.
The spectral dependence of quantum efficiency. The short-wavelength cut-off and long-wavelength tail-off correspond to the band gaps of the window and absorber materials respectively.
CONCLUSIONS

• Nano-granular amorphous indium sulfide films have been prepared using process of thermal evaporation and deposition in vacuum on glass substrates at temperatures \( T_s = 220-240 \, ^\circ\text{C} \).

• Correlations between the optical properties and the microstructure of the \( \text{In}_2\text{S}_3 \) films of various thickness have been detected. Short-wavelength shift of the band edge position upon the film thickness decreasing from 300–800 nm up to 50–30 nm has been detected and the involved mechanisms have been explained.

• Best \( \text{Cu(In,Ga)}\text{Se}_2 \) single cells on glass substrate reach 10.7 %.

• Optimization of the Ga content in \( \text{Cu(In,Ga)}\text{Se}_2 \) films and \( \text{In}_2\text{S}_3/\text{ZnO} \) technology is expected to improve \( FF \) and \( V_{OC} \) parameters and produce solar cell devices with conversion efficiencies well above 10 %. 
ACKNOWLEDGEMENTS

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