Shungite influence on the ITO-coatings basic features: mechanical, spectral, wetting parameters change

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**Transparent conductive coatings (TCC)**

**ITO**  \( \text{In}_2\text{O}_3 (90\%) + \text{SnO}_2 (10\%) \) **Indium Tin Oxide**

- **Applications**:
  - Solar cells;
  - Transparent electronics;
  - Display technology.

- **Advantages**:
  - Best transmittance values;
  - Best conductivity values;

- **Disadvantage**:
  - Very expensive.

- **Analogues**:
  - ZnO Zinc Oxide;
  - AZO Aluminum Zinc Oxide;

- **Physical parameters**:
  - Band gap 3.75 eV;
  - Charge carrier mobility 35 cm\(^2\)/V·s;
  - Refractive index 1.97..2.06.

**Figure 1** – Block diagram of the installation for the deposition of ITO films

**Figure 2** - Models of ITO [1] and ZnO [2] structures

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Shungite

Rock, the deposit of which is mainly concentrated in Karelia (region in the North-West of Russia).

Shungite nanoparticles are unique due to their:
- Non-toxic parameters;
- The ability to be easily accepted from the earth’s surface;
- Good refractive characteristics.

Table 1 - The main components of shungite

<table>
<thead>
<tr>
<th>Component</th>
<th>SiO₂</th>
<th>a-C</th>
<th>Al₂O₃</th>
<th>Crystal H₂O</th>
<th>K₂O</th>
<th>Fe₂O₃</th>
<th>S</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass composition, %</td>
<td>57</td>
<td>30</td>
<td>4</td>
<td>1.7</td>
<td>1.5</td>
<td>1.49</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

How to improve the properties of TCC?

Structuring with nanoparticles

Figure 3 – Schematic representation of the simplest LC cell (a), LC with ITO modified with shungite (b)
Transmission spectra

The shift of the transmission spectra by 40 nm to the IR region indicates:
1. Changing the band gap $E_g$;
2. A change in the mobility of charge carriers by about an order of magnitude.

$E_g$ (pure ITO) = 3.86 eV; $E_g$ (ITO+shungite) = 3.44 eV.

Figure 6 - Transmission spectra of the studied samples in the IR range (left) and the visible range (right)
Microhardness

Table 2 – Changes in the mechanical strength of ITO during structuring of CNTs and shungite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Microhardness, $10^9$ Pa</th>
<th>Increase in microhardness compared to pure ITO</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>2.2 – 2.4</td>
<td>-</td>
<td>Present work</td>
</tr>
<tr>
<td>ITO+CNTs</td>
<td>4.2 – 4.8</td>
<td>In 2 times</td>
<td>[Toikka A. S., Kamanina N. V., Zubtcova Y. A. Carbon Nanotubes as Means to Optimizing the Operation of Liquid Crystal Cells// IEEE. 2020.]</td>
</tr>
<tr>
<td>ITO+shungite</td>
<td>8.0 – 20.0</td>
<td>In 3.6 – 8.3 times</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Improvement in mechanical strength

Figure 7 - Measurement of microhardness of the sample ITO+shungite: a - surface image at a load of 1 g; b - image of the surface at a load of 5 g
Wetting parameters

Table 3 – Contact angle and free surface energy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Θy, °</th>
<th>Free surface energy, mJ/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>ITO pure</td>
<td>90.7</td>
<td>31.3</td>
</tr>
<tr>
<td>ITO+SEW</td>
<td>84.9</td>
<td>22</td>
</tr>
<tr>
<td>ITO+SEW + shungite (100 V/ccm)</td>
<td>63.4</td>
<td>27</td>
</tr>
<tr>
<td>ITO+SEW + shungite (600 V/cm)</td>
<td><strong>74.0</strong></td>
<td>9.3</td>
</tr>
</tbody>
</table>

The structure «ITO + shungite» is **hydrophilic**

Calculation of free surface energy:

$$\gamma_t \left(1 + \cos \theta_y \right) = \sqrt{\gamma_e \gamma_t} + \gamma_d$$

Θy – Young’s contact angle;
γt – surface tension;
γe – free surface energy;
γd – dispersion component;
γp – polar component.

Figure 8 – Schematic representation of a liquid drop on a solid surface
## Surface relief

### Table 4 – Sample surface roughness

<table>
<thead>
<tr>
<th>Sample</th>
<th>Roughness, nm</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 order</td>
<td>II order</td>
<td>III order</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>SD</td>
<td>Average</td>
<td>SD</td>
<td>Average</td>
</tr>
<tr>
<td>ITO pure</td>
<td>18.0</td>
<td>10.6</td>
<td>11.6</td>
<td>4.7</td>
<td>4.4</td>
</tr>
<tr>
<td>ITO+SEW</td>
<td>27.6</td>
<td>15.5</td>
<td>13.4</td>
<td>2.6</td>
<td>7.6</td>
</tr>
<tr>
<td>ITO+SEW + shungite (100 V/cm)</td>
<td>150.5</td>
<td>87.8</td>
<td>51.1</td>
<td>9.8</td>
<td>25.4</td>
</tr>
<tr>
<td>ITO+SEW + shungite (600 V/cm)</td>
<td>236.8</td>
<td>150.2</td>
<td>86.5</td>
<td>13.1</td>
<td>17.8</td>
</tr>
</tbody>
</table>

Creating relief for the alignment layer

Figure 9 – Sample surface profiles
Conclusion

1. The "ITO + shungite" system has **prospects for use in devices operating in the IR range**. There is a shift of the transmission spectrum by 40 nm towards the IR range, a significant increase in the transmission in the IR range.

2. Structuring ITO with shungite can significantly **increase the mechanical strength**.

3. Samples with shungite have more **hydrophilic** behavior.

4. Structuring ITO with shungite, as well as subsequent surface treatment with an electromagnetic wave, allows you to create an **innovative relief for orienting liquid crystal molecules**.

5. The **plans** include studying the process of increasing laser strength, changing the mobility of charge carriers and refractive properties by ellipsometry, as well as obtaining images using SEM and X-ray diffraction analysis.
Thank you for your attention!