**Study of zinc oxide thin films doped with fluorine**

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### Aim of the work

Modern devices such as flat panels, liquid crystal displays, solar cells, etc... require the use of transparent thin films presenting good electrical conductivity. Transparent conductive oxides (TCO) with large band gaps (> 3 eV) and good electrical conductivity fulfill those requirements. Due to the significant increase of the demand, the price of the most employed TCO, namely indium tin oxide (ITO) has strongly increased during the last years. Therefore, an alternative to this material becomes more and more necessary. ZnO:F is identified as the best candidate to replace ITO in TCO applications. The most used techniques for the synthesis of ZnO:F are Chemical Vapour Deposition (CVD) and Spray Pyrolysis (CSP) which both require an organometallic precursor and high temperature processing. Another drawback of these technologies is the low chemical purity of the synthesized films because of the presence of the precursor decomposition products. A promising alternative is the use of reactive magnetron sputtering for ZnO deposition which can be considered as environmentally friendly. In addition, this technique allows very fine control of the film chemistry and constitution. Therefore, the aim of this work is to study the influence of F doping on ZnO thin films deposited by magnetron sputtering.

### Experimental details

- DC reactive magnetron sputtering using a zinc target in an Ar/O2/F2 mixture.
- Film Characterization by XRD, XPS, ToF-SIMS

### Objective

- Study the incorporation of fluorine in the ZnO matrix (%F)
- Study the effect of fluorine on structural properties

### Results

#### XPS:

Adjacent is an XPS spectrum of a ZnO:F sample synthesized at 70 W, 30 mTorr, 7.5 % O2 and 0.125 % F2 in the discharge. We can identify the fluorine peak located at a binding energy of 685.1 eV that corresponds to fluorine bonded with metal atoms. Therefore, we suggest that F atoms substitute O atoms in the ZnO structure.

<table>
<thead>
<tr>
<th>Name</th>
<th>Binding Energy (eV)</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1s</td>
<td>530.84</td>
<td>40.74</td>
</tr>
<tr>
<td>Cl1s</td>
<td>284.93</td>
<td>11.52</td>
</tr>
<tr>
<td>F1s</td>
<td>685.10</td>
<td>2.41</td>
</tr>
<tr>
<td>Zn 2p3/2</td>
<td>1021.98</td>
<td>45.56</td>
</tr>
</tbody>
</table>

The ratio ZnO+F is close to 1 indicating a stochiometric compound. For most semiconductors, it is more efficient to extrinsically dope a stochiometric material rather than relying on native defects.

#### Resistivity measurement:

200 nm thin films were deposited on interdigitated gold comb. The resistivity was measured using an electrometer. Due to contact rectifiers, it is necessary to compare the data to a reference (pure ZnO coatings)

**Resistivity improved for ~ 1.5% < %F< 2.5%**

- When %F is too low → not enough charge carriers in the material
- When %F is too high → too low charge carriers mobility (loss of the crystalline structure)

#### Hall effect measurement:

 Resistivity, carrier concentration and mobility were obtained by hall effect measurement in a cloverleaf configuration according to the Van der Pauw technique. The sample were annealed in N2 at 300 °C for 15 min to ensure good electrical contact.

Resistivity of 5 x 10² Ω.cm with carrier concentration of 2.5 x 10¹⁹ cm⁻³ and mobility of 4.21 cm²/V.s have been measured for the sample containing 2 % of fluorine.

### Conclusions

In this work, ZnO and ZnO:F thin films were deposited using planar DC reactive magnetron sputtering in a gas mixture containing F2. Our XRD data reveals the decrease of the crystallite size with the increase of fluorine content. Above a fluorine concentration of 2-3%, the ZnO:F films become amorphous. Our XPS and XRD data suggests that F atoms substitute O atoms in the ZnO structure. For the optimal synthesis conditions (~ 2% of fluorine in the film), a charge carrier density of ~ 10²⁰ cm⁻³ and an electrical resistivity of 10² Ω.cm have been measured. These data are comparable to data obtain by others authors using methods like CVD [1] or CSP [2].


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