Water-based Indium Tin Oxide Nanoparticles Ink for Printed Ammonia Gas Sensor

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1. Abstract  − In this study, we characterized properties of indium tin oxide (ITO) nanoparticles dispersions mixed with suitable additives. Stable dispersion is necessary for material printing process thus optimum ratio of dispersant and surfactant is investigated. Various concentrations of nanoparticles in aqueous dispersion were studied and compared. Highly transparent thin films were fabricated by inkjet printing, deposited on a glass substrate and annealed at various temperatures. These films were tested for response to ammonia gas. A good sensing property is observed and demonstrated.

2. Keywords  − Indium tin oxide (ITO), inkjet ink, material printing, gas sensing, ammonia sensor

3. Introduction  − Nowadays, material printing technologies (involving screen-printing, roll-to-roll printing, gravure printing and ink-jet printing) are widely used especially in fabrication of solar cells, touchscreen panels and flexible displays and sensing devices for environment quality control and monitoring of diffused gasses and harmful vapours [8]. Their advantages include simplification and acceleration of fabrication processes. These low-cost technologies are based on deposition of functional material onto used substrate such as glass or transparent and flexible foils. Unlike screen printing or lithography, ink-jet printing does not require stencils or masks, therefore allowing rapid design and prototyping. The ink-jet printing technique is an interesting and versatile method to make controlled deposition of functional materials with suitable geometry on various substrates [1, 2]. Printed patterns are designed by common computer program and can be saved as simple bitmap images for printing. It is possible to use a wide range of inorganic and organic materials including inks based on metal or metal oxide nanoparticles and polymer solutions [2, 3]. The size of oxide nanoparticles, mechanical and chemical dispersion in a proper dispersion medium containing suitable dispersion stabilizers, viscosity and surface tension of the ink composition; all these are vitally important for demanded flow of droplets through the nozzles of a printing head [4].

Transparent conductive oxides (including indium tin oxide – ITO) are indispensable materials in fabrication of optoelectronic devices and can be used as a semi-conductive material for gas detecting sensors based on the resistance variation due to exposure to the target gas. Indium tin oxide (ITO) (In$_2$O$_3$:10%SnO$_2$) films have been extensively studied in recent years because they exhibit relatively rare combination of high visible transmission and significant electrical conductivity, high substrate adherence, good hardness, and chemical inertness [5]. Reducing gases for this n-type semiconductor are NH$_3$, CO, H$_2$, NO$_2$, benzene etc. During interactions between sensor and molecules of gas, surface resistivity decreases and sensitivity of detecting depends on ambient atmosphere and temperature [6]. Recent studies describe both the physical ITO deposition method [5] and chemical deposition method based on aqueous solutions [7]. In the first case, during the vapor deposition of ITO layers the high temperatures for deposition are required. In the second case, the high temperatures for annealing and sintering of particles into the compact layers are required. In this work, we describe development of ink for deposition of ITO layer and we investigate the gas sensing properties of these films printed by ink-jet technology from aqueous dispersion. The annealing temperatures are ranging from 150 °C to 600 °C, which can be suitable for flexible gas sensor printed on polymer foils.
4. Experimental

Preparation of indium tin oxide inks
ITO nanoparticles based aqueous inks were prepared in form of a mixture of indium tin oxide nanopowder < 50 nm particle size (Sigma-Aldrich product) and the optimum ratio of dispersing agent and surfactant (Disperbyk-190 and Byk-348). For modifying the density of the dispersion was selected ethylene glycol. The dispersions were mixed for several hours and before filling the cartridge were sonicated for 30 minutes by UZ Sonopuls HD 2070 homogenizer and filtered through a 0.22 µm PTFE filter to remove agglomerated particles. Concentrations of ITO nanoparticles in final inks were set to 10%, 15%, 20% and 25%.

Sensor fabrication
The thin sensoring films (15 x 15 mm) were fabricated by material inkjet printing by DMP Dimatix 2800 on cleaned (de-ionized water, acetone, ethanol) quartz substrates from one printing cycle (one layer) and the voltage at the nozzles was in the range of 23 – 26 V. Printed films were annealed at 200 °C and 400 °C in air conditions for 30 minutes. Electrodes were connected to copper wires by conductive tape.

ITO ink and films characterization and sensor response
Density and viscosity of ink were measured by Microviscometer Lovis 2000 ME and Density meter DMA 5000 M (Anton Paar). Surface tension of ITO ink was measured by Tensionmeter K100MK3 (Krüss). The surface morphology and roughness was investigated via atomic force microscopy in PeakForce mode on Atomic force microscope Dimension ICON (Bruker). The electrical conductivity of printed patterns was measured by using four-point probe (Van der Pauw method). The response to ammonia gas was measured by observing resistivity changes between “On” and “Off” sensor states at laboratory temperature (25 °C).

5. Results and Discussion

Indium tin oxide inks properties
The main properties determining good processibility by ink-jet printing are shown in Table 1. For good function of printing head, it is recommended to keep the ink viscosity between 10 and 30 cP (mPa.s) and the surface tension should be in the range from 20 to 40 N.m⁻¹ [2]. The measured data shows that the ink carries out these requirements.

The optimal amount and ratio of the two additives was determined based on the critical micelle concentration in an aqueous medium. Dissolved macromolecules of non-ionic surfactant in the dispersion medium avoid flocculation of nanoparticles by mean of steric stabilization.

Table I. Main properties of ITO inks

<table>
<thead>
<tr>
<th>Temperature = 25 °C</th>
<th>Concentration of ITO nanoparticles / w %</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension / N.m⁻¹</td>
<td>(21,58±0,08)</td>
<td>(21,61±0,08)</td>
<td>(21,64±0,08)</td>
<td>(21,67±0,09)</td>
<td></td>
</tr>
<tr>
<td>Density / g·cm⁻³</td>
<td>1,1276</td>
<td>1,1867</td>
<td>1,2419</td>
<td>1,3066</td>
<td></td>
</tr>
<tr>
<td>Viscosity / mPa.s</td>
<td>3,078</td>
<td>3,518</td>
<td>4,128</td>
<td>4,703</td>
<td></td>
</tr>
</tbody>
</table>

Annealing temperature optimization
Annealing temperature causes alignment and densification of ITO nanoparticles in the printed thin film. Effect of annealing proceeds in following steps: (i) firstly to the removal of solvent system residues at lower temperature, (ii) then it improves the contact between nanoparticles by the degradation and removal of used stabilizing polymers at moderate temperature and (iii) leads to the sintering and forming of grain at higher temperature. Larger size of grains allows better mobility of charge carriers [9]. Based on thermogravimetric analysis the annealing temperature was selected. The presence of additives could cause interaction with the gas being sensed and thus influence the response of the sensory layer. As
shown in Figure I., the last additive is vaporized at 400 °C completely. Annealing temperature for sensor devices was therefore set to the 400 °C.

**Figure I.** Thermogravimetric curves of prepared ink formula (25 w%). Decomposition of the ink proceeded in three steps. In the first two steps low-molecular substances (water and ethyleneglycol) were evaporated. Their complete evaporation was achieved below the temperature of 200 °C. Decomposition of present surfactant and dispersant agent was noted in the range from 300 to 400 °C.

*Morphology and surface roughness of ITO films*

Surface morphology was examined at three different areas of 5μm² and surface roughness (root mean square) was calculated and averaged from obtained data using NanoScope Analysis 9.1. Scan rate was 0,5 Hz and resolution 512 lines. Pictures show surface morphology of printed films.

<table>
<thead>
<tr>
<th>Concentration of ITO nanoparticles / w %</th>
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</tr>
</thead>
<tbody>
<tr>
<td>( R_{\text{rms}} ) / nm</td>
<td>( (40,7 \pm 3,4) )</td>
<td>( (30,8 \pm 0,7) )</td>
<td>( (30,8 \pm 2,1) )</td>
<td>( (34 \pm 1) )</td>
</tr>
</tbody>
</table>

**Figure II.** SEM and AFM images of ITO thin film deposited on a glass substrate and annealed at 400 °C. Various grain sizes are evident at annealing temperature of 400 °C that transmits most thermal energy to ITO nanoparticles and this phenomenon enables evaporation of additives, allows grain growth and decreases grain boundaries. Less grain boundary improves the mobility of charge carriers. Preferable structure leads to improved charge transferring and increases conductivity [9]. Granular and porous structure proved by surface roughness (as viewed in Table II.) can adsorb atmospheric oxygen easily [10].
Film resistivity and sensor response

Table III. Resistivity and thickness of printed (one cycle) thin films

<table>
<thead>
<tr>
<th>Concentration of ITO nanoparticles / w %</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness / nm</td>
<td>(548 ± 29)</td>
<td>(778 ± 21)</td>
<td>(1139 ± 30)</td>
<td>(1513 ± 43)</td>
</tr>
<tr>
<td>Rezistivity / Ω·cm</td>
<td>(51.88 ± 0.02)</td>
<td>(45.76 ± 0.03)</td>
<td>(40.37 ± 0.02)</td>
<td>(14.21 ± 0.01)</td>
</tr>
</tbody>
</table>

Figure III. Resistance measurements of ink-jet printed and annealed ITO thin films from 25 w% ink upon exposure to a) dried NH₃ gas and b) vapours over 30% ammonia solution at 25 °C.

6. Conclusions - We developed stabilized water based ITO nanoparticles ink suitable for ink-jet printing technology. This ink is applicable for deposition of conductive layers and patterns. We also demonstrated that ink-jet printed ITO thin films are sensitive for dried NH₃ gas and humidity and could be a good candidate as a printed sensor.

7. Acknowledgment – This work was supported by the Internal Grant Agency of Tomas Bata University in Zlín (grant no. IGA/CPS/2015/006) and the Ministry of Education, Youth and Sports of the Czech Republic – Program NPU I (LO1504).

8. References