Highly Sensitive Acetylene Sensing Properties of Al- and In-doped ZnO Quantum Dots

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Abstract
Acetylene (C\textsubscript{2}H\textsubscript{2}), dissolved in oil-filled power equipment, has undoubtedly the most detrimental risk in terms of safety owing to the arc discharge characteristics. It is necessary to systematically detect the dissolved acetylene gas for optimum operation condition which can directly affect the safety and stability of the power system. In this vein, we report the high-performance C\textsubscript{2}H\textsubscript{2} gas sensor based on 1 at\% In-doped ZnO quantum dots (QDs) which was synthesized by a hydrothermal method. The phase and morphology of the as-synthesized QDs were characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM) analyses. The sensing properties of the C\textsubscript{2}H\textsubscript{2} gas were carried out by exposing the sensor to various concentration under the various working temperatures. The response to the 10 ppm acetylene was \textasciitilde 314 in air and \textasciitilde 570 in N\textsubscript{2} at the optimum operating temperature, which are superior to that of other previously reported C\textsubscript{2}H\textsubscript{2} sensors based on semiconducting metal oxides.

Key words: acetylene gas sensor, In-doped ZnO, quantum dots, transformer oil

Introduction
One of the most challenging ongoing issues in power transformers is the monitoring of degradation in the internal components of a transformer. When the oil-filled transformer is under abnormal stress, it can lead to the chemical breakdown of the oil or cellulose, disenable the dielectric insulation. The failure to transfer leads to the evolution of a mixture of gases, including hydrogen (H\textsubscript{2}), hydrocarbons (CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}), and carbon oxides (CO, CO\textsubscript{2}). Detection of the generated gases can be one of the markers to diagnose the failure or predict the lifespan of a transformer. Among the gases that can be generated in transformer oil, C\textsubscript{2}H\textsubscript{2} is the most important gas to be monitored in a transformer due to its characteristic to evolve during arc discharge, which leads to the catastrophic accidents of a transformer [1]. In this work, we report the highly sensitive C\textsubscript{2}H\textsubscript{2} sensing performance of Al- (AZO) and In-doped (IZO) ZnO QDs. The comparison of sensing performance with previously reported results in other groups and the sensing mechanism are addressed.

Results and Discussion
Un-doped ZnO (ZO) and doped (Al, In) ZnO QDs were synthesized by a wet chemical method as described in our previous reports [2]. Figure 1(a) shows a schematic image of an actual sensor device composed of Pt electrodes interdigitated on a SiO\textsubscript{2} substrate via a photolithography method. Figure 1(b) presents the TEM image of the as-synthesized IZO QDs.

Fig. 1. (a) Schematic illustration of the sensor device; (b) TEM image of actual 1 at\% In-doped ZnO QDs; (c) XRD patterns of un-doped, Al-, and In-doped ZnO QDs.
In the magnified position of the device in Fig. 1(a), a ZnO QD layer is deposited on top of the Pt electrodes. The XRD patterns confirm that the nanocrystals are of crystallinity with the typical hexagonal wurtzite crystal structure ZnO (see Fig. 1(c)). The broadening of the peaks in the XRD patterns can be attributed to the small particle size (~5nm) of the as-synthesized ZnO QDs. 

The real-time electrical resistance of ZO, AZO, and IZO QDs were measured at various C2H2 concentrations in air and N2, respectively. The sensing response of the C2H2 gas is defined as $R_a/R_g$, where $R_a$ and $R_g$ are the resistance of the sensors in air (N2) and in the environment containing acetone, respectively.

![Image](image_url)

Table 1. Sensing properties of various metal oxide semiconductor gas sensors to C2H2 (S=sensitivity (response/ppm); L=low detection limit; $t_R$=response time; $T_{opt}$=optimal working temperature)

<table>
<thead>
<tr>
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<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>7.9</td>
<td>1.0</td>
<td>0.14</td>
<td>0.12</td>
<td>31.4</td>
</tr>
<tr>
<td>L (ppm)</td>
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<td>1</td>
<td>1</td>
<td>3</td>
<td>0.1</td>
</tr>
<tr>
<td>$t_R$ (s)</td>
<td>15</td>
<td>5</td>
<td>2</td>
<td>57</td>
<td>5</td>
</tr>
<tr>
<td>$T_{opt}$ (°C)</td>
<td>420</td>
<td>250</td>
<td>206</td>
<td>200</td>
<td>500</td>
</tr>
</tbody>
</table>

Fig. 2. Variation in sensing responses of ZO, AZO, IZO QDs at 10 ppm C2H2 under their optimal operating temperatures in (a)-c) air and (d)-(f) N2, respectively.

Figure 2 shows the variation in responses of ZO, AZO, and IZO QDs to 10ppm C2H2 under optimized working temperature in air and N2, respectively. In both air and N2, a higher sensing performance is observed with AZO QDs compared to ZO QDs and with IZO QDs compared to AZO QDs. This is due to the replacement of the Zn2+ cation by Al3+ and In3+, which act as a donor, leads to formation of active adsorption sites which favor the adsorption of oxygen species.

The best sensing response is observed in IZO QDs. The maximum responses of IZO QDs are ~314 in air and ~570 in N2 which is superior to that of other previously reported C2H2 sensor based on semiconducting metal oxides [3-6]. This can be attributed to a greater number of absorbed oxygen ion species, providing more active adsorption sites, in IZO QDs compared to ZO and AZO QDs. The response as a function of C2H2 concentrations and analyses from X-ray photoelectron spectroscopy (XPS), UV–visible spectrophotometry (UV-vis), and Brunauer-Emmett-Teller (BET) are presented in detail.

References


[5] Ying Lin, Chao Li, Wei Wei, Yujia Li, Shanpeng Wen, Dongming Sun, Yu Chen and Shengping Ruan, A new type of acetylene gas sensor based on a hollow heterostructure, RSC Adv., 2015, 5, 61521, DOI: 10.1039/C5RA10327D