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

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Abstract

Acetylene (C_2H_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_2H_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_2H_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 ~314 in air and ~570 in N_2 at the optimum operating temperature, which are superior to that of other previously reported C_2H_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, disenabling the dielectric insulation. The failure to transfer leads to the evolution of a mixture of gases, including hydrogen (H_2), hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6), and carbon oxides (CO, CO_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_2H_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_2H_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.

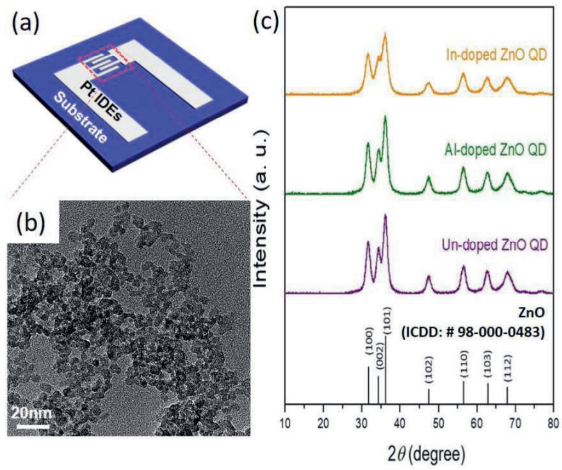

Fig. 1. (a) Schematic illustration of the sensor device; (b) TEM image of actual 1 at% In-doped ZnO QDs; (c) XRD patterns of un-doped, Al-, and In-doped ZnO QDs.

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_2 substrate via a photolithography method. Figure 1(b) presents the TEM image of the as-synthesized IZO 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 C_2H_2 concentrations in air and N_2, respectively. The sensing response of the C_2H_2 gas is defined as $(R_a-R_g)/R_g$, where R_a and R_g are the resistance of the sensors in air (N_2) and in the environment containing acetone, respectively.

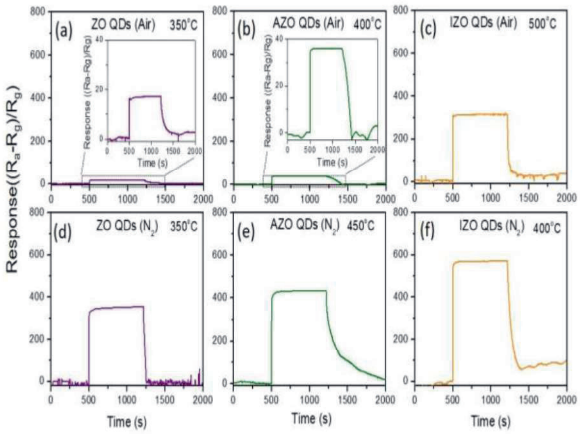

Fig. 2. Variation in sensing responses of ZO, AZO, IZO QDs at 10 ppm C_2H_2 under their optimal operating temperatures in (a)-(c) air and (d)-(f) N_2, respectively.

Figure 2 shows the variation in responses of ZO, AZO, and IZO QDs to 10ppm C_2H_2 under optimized working temperature in air and N_2, respectively. In both air and N_2, 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 Zn^{2+} cation by Al^{3+} and In^{3+}, 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 N_2, which are superior to that of other previously reported C_2H_2 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 C_2H_2 concentrations and analyses from X-ray photoelectron spectroscopy (XPS), UV–visible spectrophotometry (UV-vis), and Brunauer-Emmett-Teller (BET) are presented in detail.

Table. 1. Sensing properties of various metal oxide semiconductor gas sensors to C_2H_2 (S=sensitivity (response/ppm); L=low detection limit; t_R=response time; T_{opt}=optimal working temperature)

	[A]	[B]	[C]	[D]	[E]
S	7.9	1.0	0.14	0.12	31.4
L (ppm)	1	1	1	3	0.1
t_R (s)	15	5	2	57	5
T_{opt} (℃)	420	250	206	200	500

[A] An ZnO microdisks [3]

[B] Ni-doped ZnO nanoflowers [4]

[C] NiO/SnO_2 heterostructures [5]

[D] Ag/ZnO Hrc-RGO hybrid [6]

[E] IZO QDs (this work)

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