Linearly resistive humidity sensor based on quasi one-dimensional ZnSe nanostructures

Y.P. Leung, Wallace C.H. Choy *, T.I. Yuk

Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong

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A B S T R A C T

A resistive-type relative humidity sensor based on one-dimensional ZnSe nanostructures is reported. The sensor is fabricated by a two-step thermal evaporation – first the growth of a polycrystalline ZnSe substrate and then the growth of ZnSe nanowires. Ohmic contacts have been made to the sensor by simple silver painting. The sensor has a linear response of relative humidity over the range of 11.3–97.3%, which offers better sensitivity than the commonly reported exponential response, particularly at low relative humidity below 20%. A model based on capillary condensation is given to explain this feature.

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1. Introduction

One-dimensional (1D) semiconductor nanostructures have attracted much attention recently due to their interesting size-dependent electronic and optical properties. Moreover, 1D semiconductor nanostructures give great prospects in realizing future electronic and photonic applications in nanoscale [1]. In last few years, morphology controls of fabricating 1D nanostructures such as wires [2], tubes [3], belts [4], and rings [5] have been the strong focus of attention for the applications in field-effect transistors [6], inverter [7], photodetectors [8] and chemical sensors [9]. While materials like ZnO, ZnS, CdSe and CdS have been the focus of majority researches of II–VI semiconductors, only limited number of reports on 1D ZnSe can be found in literature [10].

ZnSe, a wide bandgap II–VI semiconductor has been used in optoelectronic devices such as laser diodes [11] and solar cells [12]. Besides, gas sensing based on the photoluminescence (PL) of the ZnSe nanowires in different gas ambient had been reported [13]. Moisture sensing is also an important area in sensor researches of industrial, environmental, and clinical sectors. Many reports of humidity sensors are based on porous ceramics [14]. Recently, 1D nanostructures have also been demonstrated to be applicable in humidity sensing [15,16]. In this Letter, we investigate the relative humidity (RH) sensing ability based on 1D ZnSe nanostructure. Ohmic contacts have been made to the sensor by using simple silver painting. Moreover, our sensor offers a linear response over the range of 11.3–97.3%, which is different from and has better sensitivity than the exponential response commonly reported for humidity sensors. The reason of this phenomenon will be discussed.

2. Experiment

The humidity sensor was fabricated in two steps – growth of polycrystalline ZnSe substrate and growth of ZnSe nanowires. Both the substrate and the nanowires were grown by thermal evaporation method. First, a polycrystalline ZnSe film was fabricated in a two-zone tube furnace. About 2 g of ZnSe powder (99.99%, Aldrich) was placed into a cleaned alumina boat and then loaded into the temperature zone at the upstream of the furnace. Then the system was evacuated for 1 h and purged with the carrier gas (95% Ar + 5% H2) for another hour to remove residual oxygen. After that, the system was pumped down to a base pressure of about 10−3 torr and the carrier gas was then fed into the tube furnace with a constant flow rate of 600 sccm (standard cubic centimeter per minute). Only one temperature zone was used for the growth of the ZnSe film. Upon steady pressure and flow rate, the temperature of the zone where the ZnSe source was placed was raised from room temperature to 950°C and maintained for 3 h, while the other temperature zone was remained power off during the growth of the film. At the end of the growth process, the furnace was gradually cooled down to room temperature. Polycrystalline ZnSe film was collected at the quartz tube wall at the region about 10–20 cm downstream from the ZnSe source.

A small piece of the as-grown ZnSe film (~1 cm × 1 cm) was then used as the substrate to grow ZnSe nanowires. Adopting the vapor–liquid–solid growth mechanism for 1D nanostructures, about 5 nm thick of gold was sputtered onto the substrate as the catalyst for the growth of nanowires. About 0.5 g ZnSe was loaded into an alumina boat and placed at the upstream temperature zone. The gold coated substrate was firstly placed on a cleaned alumina plate and then positioned at the downstream temperature zone. The system was evacuated and purged in the same way as described previously. After that, the pressure and the flow rate of
the carrier gas were set to 100 torr and 200 sccm, respectively. The growth of the nanowires lasted for 30 min.

The sample collected after the growth was then glued onto a cleaned glass and two electrodes were made by silver painting (RS Components) with contact area about 1.5 mm$^2$ and 1 cm. The growth of the nanowires lasted for 30 min.

The sample collected after the growth was then glued onto a cleaned glass and two electrodes were made by silver painting (RS Components) with contact area about 1.5 mm$^2$ and 1 cm. The current–voltage ($I$–$V$) characteristic of the sample was measured by using Keithley 2400 sourcemeter at different RH at room temperature. Environments of different RH were prepared by equilibrium saturated salt solutions – LiCl(aq), MgCl$_2$(aq), Mg(NO$_3$)$_2$, NaCl(aq), and K$_2$SO$_4$(aq), corresponding respectively to a RH of 11.3%, 32.8%, 52.9%, 75.3% and 97.3%. The morphology and the composition of the sample were measured in a Field Emission Scanning Electron Microscope (FE-SEM, Leon 1530) equipped with an Energy Dispersive X-Ray Spectroscopy (EDX). The sample structure was characterized by X-Ray Diffraction (XRD) using CuK$_\alpha$ radiation. The sample structure was characterized by X-Ray Diffraction (XRD) using CuK$_\alpha$ radiation. The PL spectrum was measured with a He–Cd laser of a 325 nm line excitation.

3. Results and discussion

Fig. 1a shows the SEM image of the ZnSe film. It is clear that the film is formed by many crystals with a typical diameter of a few hundreds of nanometers. The inset of Fig. 1a shows the XRD of the ZnSe film, in which the zinc-blende (ZB) structure is confirmed since only ZB structured ZnSe peaks are observed. After the second step of growth, ZnSe nanowires are formed on the ZnSe film as shown in Fig. 1b. The EDX spectrum of the sample as shown in the inset of Fig. 1b confirms that the sample has a composition of only Zn and Se with about 1:1 ratio.

The $I$–$V$ characteristics of the sample at different RH are shown in Fig. 2. Since the current for the case of RH = 97.3% is relatively large, a separate plot is given in the inset of Fig. 2 for better illustration. One can notice the linear behavior of the $I$–$V$ curves at various RH. However, when a metal and a semiconductor are brought into contact, a Schottky Barrier will be normally formed. Such a barrier will result in high-resistance rectifying (i.e., nonlinear $I$–$V$) contacts and is usually not desirable. To avoid the rectifying feature, Ohmic contacts are essential [17–19]. In our experiment, the Ohmic contacts of the sample are made by simple silver painting. It should be noted that when Ag and ZnSe are brought into contact, a barrier height ranging from 0.76 to 1.45 eV [20,21] will be formed. However, the linear $I$–$V$ characteristics here clearly show the Ohmic behavior of the contacts. The phenomenon can be attributed to the unintentional doping of the polycrystalline ZnSe substrate as indicated by the PL spectrum below. The PL spectrum was measured with a He–Cd laser of a 325 nm line excitation.

Fig. 3 shows the PL spectrum of the ZnSe film measured at 10 K. In the spectrum, only the donor–accepter transition peak at 2.68 eV and two deep level peaks at 1.95 and 2.27 eV can be observed. For an undoped ZnSe single crystal, a near band edge emission (NBE) peak at about 2.8 eV is usually observed [22]. The absence of this peak here suggests a high level of impurities incorporated into the ZnSe which results in the quenching of the NBE peak. The absence of this peak here suggests a high level of impurities incorporated into the ZnSe which results in the quenching of the NBE peak [23] and offering the Ohmic behavior. Possible source of the unintentional doping is most likely comes from the impurities in the ZnSe source. According to the Certificate of Analysis of our ZnSe source (Sigma-Aldrich LOT 14123AE), 6.8 ppm (parts per million) of Cu and 1.8 ppm of Na are found in the 99.99% ZnSe. Therefore we can associate the 2.68 eV and the 2.27 eV peaks with Na [24] and Cu [25] doping, respectively, while the deep level 1.95 eV peak is usually known as the self-activated peak. Further investigation is needed in order to control the dopants concentrations. This can be done by using a more pure ZnSe source together with controlled among of Na and Cu impurities.

Fig. 4 shows the response of the sample upon steam pulses. The operating voltage is fixed at 1 V. The response of a polycrystalline ZnSe film without ZnSe nanowires and a bare glass are also shown...
It can be seen that the sensitivity (in terms of the current flow through the sample upon the steam pulses) of the sample with ZnSe nanowires is about 10 times higher than that of the sample without nanowires, and about 30 times higher than that of the bare glass. Fig. 5 shows the resistances of the sample measured at different RH. The resistance decreases with increasing humidity which implies the ionic-type humidity sensing mechanism [14]. The RH sensing ability of the ionic-type humidity sensors can be understood by the proton transfer within the aquatic layer of the adsorbed water molecules on the sensor surface due to the Grothuss mechanism [26].

One interesting result to be pointed out is the linear relationship between the resistance and RH. For an ionic-type humidity sensor, the resistance usually decreases with a roughly exponential trend to RH [14] which makes the sensor less sensitive in low humidity and is an important issue for the low RH sensing. The conductivity of the sensor depends on the amount of water molecules adsorbed onto the surface. The more the water molecules are adsorbed, the higher the conductivity. Theoretically, the growth rate of the liquid water from vapor phase, which directly relates to the number of water molecules adsorbed, should vary linearly with RH at a given temperature [27]. Therefore, one should expect a linear change of resistance with RH. Nevertheless, it has been found that one monolayer of water will be adsorbed onto a surface at RH of about 20% [16]. This means that only few layers of water molecules can be adsorbed onto the sensor surface at low RH. Indeed, the first chemisorbed water layer and the first physisorbed water layer are immobile [26]. As a result, the resistance of the sensor will be very high at low RH, which makes humidity sensors based on this protonic conduction would not be quite sensitive at this RH range.

From this discussion, we should expect the resistance of the sample measured at RH lower than 20% should go up. However, as shown in Fig. 5, the resistance of the sample measured at 11.3% RH remains linear. We suggest the reason for such linearity at low RH is due to capillary condensation.

For the sample with nanowires, the water adsorption is induced and enhanced by the capillary condensation which occurs between the voids of the nanowires. For randomly grown nanowires, one can treat the numerous and irregular voids in between the nanowires as interconnecting capillary pores which increase the surface areas for the adsorption of water molecules. Capillary condensation occurs in those pores up to a size of $r_k$ at a particular relative humidity and temperature. The value of $r_k$ is given by the Kelvin equation [14]

$$r_k = \frac{2 M}{\rho RT \ln \left( \frac{P}{P_s} \right)}$$

where $P$ is the water vapor pressure, $P_s$ is the water vapor pressure at saturation, $\rho$ and $M$ are the surface tension, density and molecular weight of water, respectively.

Due to the dense and small capillary pores formed by the nanowires, capillary condensation can take place more easily at low RH such that not only a few immobile water layers but also sufficient layers of water can be adsorbed on the sensor at RH of 11.3%. Even though there are no available salts for preparing the equilibrium saturated salts solutions for lower RH in our experiments, it is expected that the resistance will eventually change exponentially as usually reported [14] at lower RH because of the absence of mobile water layer.

4. Conclusion

A linear resistive humidity sensor based on ZnSe nanowires has been demonstrated. The Ohmic contacts of the sensor are achieved by unintentional high level doping of the polycrystalline ZnSe substrate. The humidity response of the sensor reported here is linear over the RH ranging from 11.3% to 97.3%. The reason of the linearity at low RH is attributed to capillary condensation occurs at low RH.
due to small voids formed by networks of nanowires. Because the sensing mechanism of the ionic-type humidity sensor relies on surface effects, the control of porosity and surface activity is the fundamental concern for sensor fabrication. The use of nanowires reported in this Letter demonstrates an opportunity in controlling the onset of capillary condensation, which extends the sensibility at low RH.

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References