

Enhancement of Zn_{1-x}Cd_xO Nanowires Sensor Performance through Cd-Doping

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Abstract — Metal oxides such as zinc oxide have been studied intensively as H₂ sensors during of the last decade. Zn_{1-x}Cd_xO is a material which presents new properties at nanometer dimensions. This work demonstrates an enhanced sensitivity performance of multiple Zn_{1-x}Cd_xO nanowires-based sensor structures prepared by screen-printing technique for the detection of hydrogen at room temperature. Through Cd doping, the gas response and recovery times of multiple Zn_{1-x}Cd_xO nanowires to H₂ has been improved. It is shown that cadmium-doping in single-crystal zinc oxide nanowires can be used to optimize their response to gases without the requirement of external heaters.

Index Terms — Zn_{1-x}Cd_xO, nanowires, sensor, hydrogen.

I. INTRODUCTION

Hydrogen (H₂) sensors are extensively used as detector in biological systems, combustion systems, as well as in the chemical, petroleum, or semiconductor industries [1-2]. Nanostructures show great potential for sensorial nanodevice applications [3-8] due to large surface to volume ratio and controlled flow of confined charge carriers. For example, Cd-doped ZnO nanowires have been used in LED devices and sensing nanodevices [3-4,9-10].

Nano-ZnO-based H₂ sensors have been reported previously [5-8]. For example hydrogen-selective sensing in nano-ZnO based sensors was reported on pure and Pt-coated multiple ZnO nanorods [11-12], ZnO nanorod arrays and networks [13-14], individual nanorod/nanowire ZnO [5-7], and SnO₂-coated ZnO nanorods [15]. However, for industrial production purposes, a cost-effective and efficient synthesis process is required [9,16]. Although, previous publications on ZnO nanowire/nanorod-based H₂ sensors showed the promise of such devices in commercial sensing applications, their relative slow response and recovery times are major drawbacks for their implementation in an industrial setting. Current demands on chemical nano-sensors require enhanced gas sensitivity, selectivity, stability and faster gas responses. Improvements in the performance of nanowires-based sensors can be achieved via doping or surface functionalization.

In this work we used an electrochemical method for the synthesis of Cd-doped/alloyed ZnO nanowire array. Samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and gas sensing response. By using screen printing technique Zn_{1-x}Cd_xO nanomaterial were integrated into a sensor-device structure and its response to H₂ at room temperature measured. It was

found a reduction of the sensor operation temperature and enhancement of their gas response were observed.

II. EXPERIMENTAL

The Zn_{1-x}Cd_xO nanowire arrays were grown on F-doped tin oxide (FTO) film supported on a glass substrate, with a sheet resistance of 10 Ω/sq by electrochemical deposition [9-10]. The following parameters were used during the electrodeposition: an electrical potential of -1 V vs SCE, a total charge per unit area of -10 C·cm⁻², a deposition temperature of 92 °C [9-10,17], and a total growth time of 150 min. After deposition, the samples were rinsed with deionized water, dried in air, and thermal annealed in air at 300 °C for 11 h.

SEM images were acquired with an Ultra 55 Zeiss FEG at an acceleration voltage of 10 kV. The synthesized structures were characterized with a high-resolution X-ray diffractometer (Siemens D5000) operated at 40 kV and 45 mA using CuK_{α1} radiation (λ = 1.5406 Å). Details of the experimental procedures can be found in our report [17].

Further analysis of the chemical composition of the synthesized samples was conducted via secondary ion mass spectrometry (SIMS) with a Physical Electronics ADEPT 1010 quadrupole analyzer with a 3 keV Cs⁺ primary beam at 60° from normal direction.

The sensors were made by screen-printing technique and contacted with Al as contact electrodes. This method can be applied to the fabrication of nanowires -based sensor structures. The characteristic H₂ response of a sensor structure was studied at room temperature (RT, 22°C). The measuring apparatus consisted of a closed quartz chamber connected to a gas flow system [5]. The humidity of the gas mixture was kept at about 53% relative humidity (RH) at RT. The concentration of test gases was measured using a pre-calibrated mass flow

controller. Hydrogen and air were introduced to a gas mixer via a two-way valve using separate mass flow controllers. The test gases were allowed to flow to a test chamber with a sensor holder, in which the nanosensor was placed. By monitoring the output voltage across the nanowire-based sensor, the changes in the resistance were measured in air and in a test gas. A computer with suitable LabView interface handled all controls and acquisition of data. All measurements were performed in a quasi-steady state.

III. RESULTS AND DISCUSSIONS

Figure 1(a) presents a SEM image of a quasi-aligned high aspect ratio Cd-doped $Zn_{1-x}Cd_xO$ nanowire array grown by electrodeposition ($6 \mu M CdCl_2$) on a FTO substrate. It can be seen that these nanowires have uniform lengths of about $2 \mu m$ and diameters of $50\text{--}200$ nm. $Zn_{1-x}Cd_xO$ nanowires possess hexagonal cross-sections exhibiting $\{100\}$ planes on the sides (not shown). The aspect ratio (length/width) of the doped $Zn_{1-x}Cd_xO$ nanowire is about 30 [9]. Insert in Fig. 1(a) shows cross-sectional view of $Zn_{1-x}Cd_xO$ nanowire array grown by electrodeposition ($10 \mu M CdCl_2$) on a FTO substrate. It was observed an increase in nanowire diameter and its shape was changed due to higher alloying level.

A low-magnification TEM image of transferred $Zn_{1-x}Cd_xO$ nanowires with uniform diameter is presented in Figure 1b. A TEM image of nanowires showing an uniform diameter is presented in Figure 1b. A high-resolution TEM image taken from the edge of an individual nanowire indicates a single crystal structure, do not display any noticeable defects, and are oriented along the $\langle 0001 \rangle$ c -axis, Figure 1c. The measured lattice spacing ($c = 5.2055 \text{ \AA}$) corresponds to that of $Zn_{1-x}Cd_xO$ crystalline planes [9]. However, ZnO and CdO can normally be found in two different stable crystal structures - wurtzite (wz) and rocksalt (rs), respectively, which complicates the fabrication of single-phase structures in a broad compositional range [18]. Previous detailed analysis of diffraction and photoluminescence PL data revealed that the wurtzite single-phase stability range is likely to be as narrow as 0–2% Cd in ZnCdO [18]. The HRTEM image (Figure 1c) reveals that the $Zn_{1-x}Cd_xO$ nanowires ($6 \mu M CdCl_2$ in the bath) are uniform and single crystalline in the investigated area. According to our TEM observation, we conclude that highly crystalline Cd-ZnO NWs with hexagonal structure can be successfully synthesized at low temperature by electrodeposition method as previously reported in our reports [9-10].

Figure 2 shows the X-ray diffraction XRD pattern recorded in the range of $10\text{--}90^\circ$ with a scanning step of 0.02° of $Zn_{1-x}Cd_xO$ nanowires with high-aspect ratio. XRD studies of the crystal structure indicate only zinc oxide peaks, along with the reflections from the FTO substrate for samples grown with lower concentrations of Cd in the bath ($<6 \mu M CdCl_2$). The pattern matches the lattice spacing of crystalline zinc oxide in the wurtzite structure (space group: $P6_3mc(186)$; $a = 0.3249$ nm, $c = 0.5206$ nm). The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS)

card for ZnO (JCPDS 036-1451). It can be seen that XRD pattern from this sample shows predominant (002) diffraction peaks [9]. The lattice constants of pure bulk ZnO are $a = 3.249 \text{ \AA}$ and $c = 5.206 \text{ \AA}$ [9], and those of pure ZnO nanorods (wurtzite structure) $a = 3.2506 \text{ \AA}$, $c = 5.2055 \text{ \AA}$ [7]. However, larger lattice parameters were obtained for the doped $Zn_{1-x}Cd_xO$ nanowires for Cd concentrations in the electrolyte of 2 and $6 \mu M$ ($a = 3.2507 \text{ \AA}$ and $c = 5.207 \text{ \AA}$) [9]. The XRD shows overexpression of the (002) plane suggesting a preferential growth with the c -direction perpendicular to the substrate for most of the NWs. These studies are in accordance with SEM observations (Fig. 2).

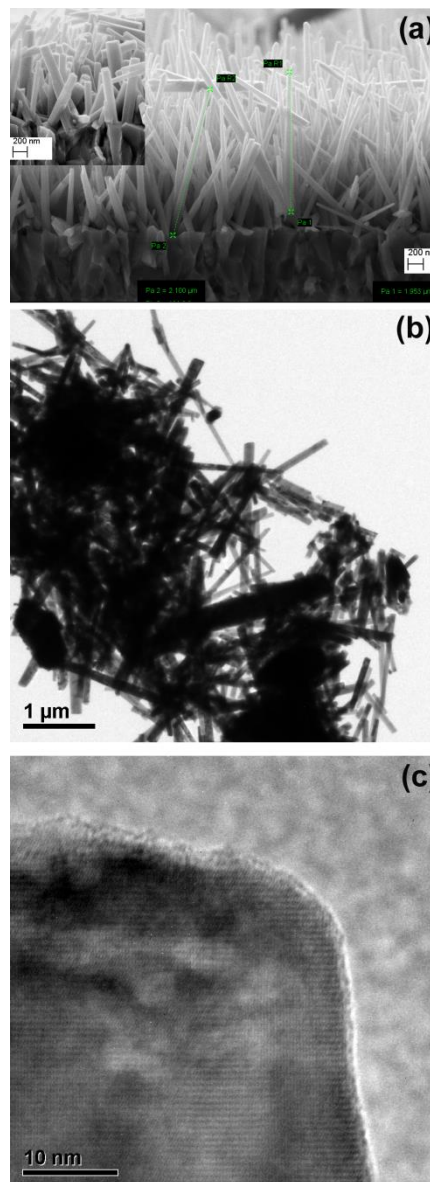


Fig. 1. (a) SEM image of $Zn_{1-x}Cd_xO$ nanowires deposited on FTO substrate ($6 \mu M CdCl_2$ in the bath). Insert is a SEM image of $Zn_{1-x}Cd_xO$ nanowires grown by electrodeposition ($10 \mu M CdCl_2$ in the bath). (b) Transferred $Zn_{1-x}Cd_xO$ nanowires from initial FTO substrate. (c) TEM image of taken from the edge of an individual nanowire from (a). These nanowires were used as building nanoblocks for sensors structures.

In the XRD patterns of $6.0 \mu M$ Cd-alloyed ZnO nanowires, CdO peaks were detected [9]. Such CdO peaks were observed more pronounced in samples with x higher than 0.12, for higher concentrations of Cd in the bath (>6

$\mu\text{M CdCl}_2$). In all samples wurtzite zinc oxide peaks were clearly detected, which means that the dopant does not change the wurtzite structure of material for low concentrations of Cd(II) in the bath. The change of full width at half maximum from 0.109° (pure ZnO) to 0.085° ($6 \mu\text{M Cd-ZnO}$) of the (002) peak is in agreement with previous SEM [9] showing the decrease in the diameter of the NWs grown in $6 \mu\text{M CdCl}_2$ in the bath compared with ZnO. The qualities of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ were demonstrated by the stoichiometric composition deduced from the EDX analysis as well as by the XRD crystallographic data (see [9]). The x in $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ was computed and presented in our previous work [9].

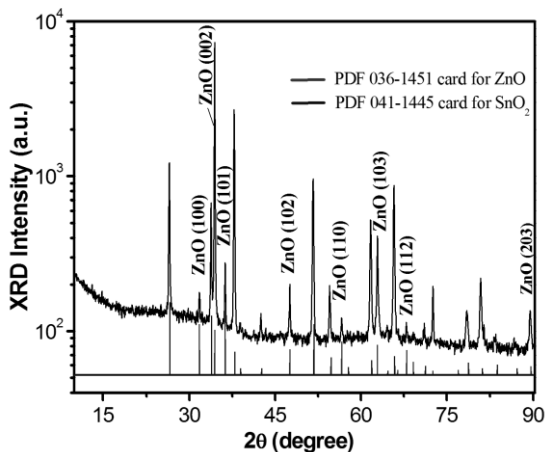


Fig. 2. XRD patterns of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires ($2.0 \mu\text{M Cd}$ in the bath) deposited on FTO substrate.

The chemical composition of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires was investigated by SIMS. Figure 3 shows Zn, Cd and Sn signals from the Cd ($6 \mu\text{M}$)-doped ZnO NW on FTO versus the sputtering time. The Cd count rate seems to closely follow the Zn count rate over most of the investigated sample depth. This is an indication that the Cd dopant has been evenly incorporated into the ZnO nanowire structure as was reported previously [9]. As expected, no correlation between the Cd and Sn (from the FTO substrate) count rates was observed, and a gradual increase in the Sn signal is observed as a function of the sputtering time until saturation is reached. The detailed experiments on SIMS for Cd doping can be found in previous works [9-10].

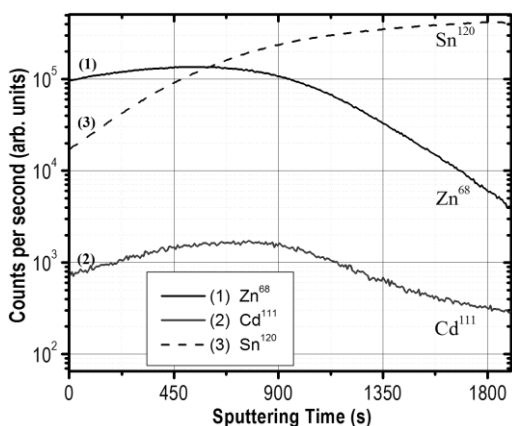


Fig. 3. SIMS measurements of Cd ($6 \mu\text{M}$)-doped ZnO. The dashed curve (Sn) corresponds to the FTO substrate.

$\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires were released from an array of as-grown NWs (see Fig. 1a) by sonication in ethanol, and subsequently transferred to a glass substrate or by a direct contact technique of the sample with a clean Si wafer. Several devices were fabricated using $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires (see insert in Fig. 4) with lengths between 2 and $3 \mu\text{m}$ and radii between 50 nm and 150 nm, which showed reproducible electrical responses. The current-voltage curves of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires-based sensor structures measured at 300 K show a linear behavior (not presented). The single NW dark-resistance of $\sim 6 \text{ k}\Omega$ in air at atmosphere pressure [9] is assigned to oxygen molecules and water molecules adsorbed on the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires surface, which are expected to capture free electrons [5] as well as to the protonic conduction on the surface. The higher resistance $\sim 10 \text{ M}\Omega$ of multiple $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires-based sensor structures is assigned to oxygen molecules adsorbed on the nanowires surfaces, which are expected to capture more free electrons and principally to intergrains barriers for charge carriers. Figure 4 shows the transient gas response ($|R_a/R_g| \times 100\%$) of multiple $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires-based sensor structures upon exposure to 100 ppm of H_2 gas at RT. As can be seen in Figure 4, both, response (τ_r) and recovery times (τ_f) ($\tau = |t_{90\%} - t_{10\%}|$) were very fast for the sensor, taking 3 and 6 s for 90% full response and recovery, respectively. It can be seen a larger and quicker gas response in the case of the doped nanowires sensor in comparison with pure ZnO reported in [5,7,19]. The changes in the resistance of the sensor after exposure to hydrogen return to within 10% of the initial value in about 5-6 s for the doped sample. This is explained by the presence of adsorbed gas molecules, which are desorbed from the surface of the doped nanostructure faster than in the case of pure ZnO nanowire reported previously [5,7]. Usually, operation at elevated temperature or UV light pulses are used in order to desorb the gas species from the surface of the sensor material [5]. In our case, the larger surface-to-volume ratio of the single-crystalline nanowires offers potential to improve the gas response and selectivity for hydrogen. The proposed sensing mechanism will be discussed in details in a forthcoming paper.

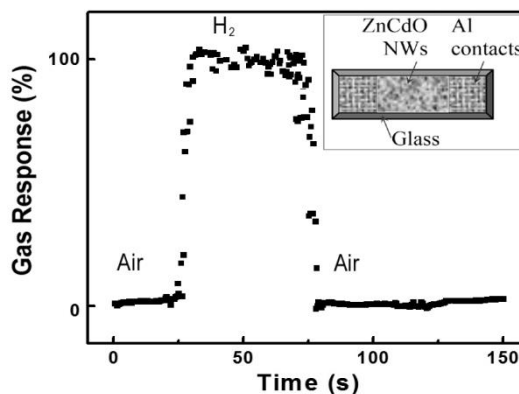


Fig. 4. Room temperature gas response of multiple $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ ($6 \mu\text{M}$) nanowires-based sensor structures. In all cases, a 100 ppm H_2 gas pulse was used. Insert shows the schematic illustration of the investigated sensor structure with multiple $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ nanowires and Al contacts.

The gas response of the resistive sensors under ambient conditions can be given by the following equation [5]:

$$S = \left| \frac{G_a - G_g}{G_g} \right| \cdot 100\% = \left| \frac{4}{D} (\lambda_{D(a)} - \lambda_{D(g)}) \right| \cdot 100\%$$

(1)

where G_g and G_a are the conductance of ZnO nanowires in H₂ gas and in air ambient, respectively, λ_D - the Debye length/radius. It can be seen that S depends on λ_D and $1/D$. The extent of the space-charge layer, which controls the electrical conductivity in the nanowires depends on the Debye length and the interfacial potential energy.

IV. CONCLUSION

Multiple Zn_{1-x}Cd_xO nanowire-based sensors were fabricated using screen-printing technique. Our device structure demonstrated sensitivity and fast response time to H₂ (down to 100 ppm) and improved response/recovery times in comparison with previous results of pure ZnO nanowire-sensors.

A dependence of the gas response of multiple Zn_{1-x}Cd_xO nanowires-based sensors was observed versus Cd-doping in nanowires grown by electrochemical method. In particular, Zn_{1-x}Cd_xO nanowires showed faster gas response. Additionally, the gas response time was significantly improved as compared to previous related reports for undoped ZnO. Adding a 6 μ M CdCl₂ in the electrolyte during ECD permits to growth nanowires improved hydrogen response time. The fact that our sensors require extremely low power to operate represents an important advance in power efficiency and nano-miniaturization. This is an important step toward low power and faster gas sensing nano-devices. In summary, we have demonstrated that cadmium-doping in single-crystal zinc Cadmium oxide Zn_{1-x}Cd_xO nanowires can be used to optimize their response to gases without the requirement of heaters.

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