MATERIALS
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Gas sensing capability of spray deposited Al-doped ZnO thin films

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Abstract. Aluminium-doped zinc oxide thin films were deposited from zinc acetylacetonate and aluminium acetylacetonate at various aluminium concentrations and deposition temperatures by ultrasonic spray pyrolysis. The structural and morphological properties and elemental composition of these films were studied by X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray spectroscopy, respectively. The gas sensing properties were studied by a two-point probe in O_2/99% N_2 and H_2/97% Ar at operating temperatures of 60, 80, and 100 °C. The films were composed of hexagonal wurtzite-type zinc oxide. The surface morphology of the films depends on the amount of aluminium doping. The hydrogen sensing capability of aluminium-doped zinc oxide thin films deposited from 5 at% Al/Zn solution decreased from 11% to 5.5% as deposition temperature was increased from 280 to 400 °C, but the stability improved by an order of magnitude. The highest sensor response (8%) to 3 vol% H_2 in Ar was observed at an operating temperature of 100 °C in the film deposited at a substrate temperature of 400 °C from the solution containing 2 at% Al/Zn. Aluminium doping above 2 at% Al/Zn in the solution reduced film resistance by up to two orders of magnitude and sensor response decreased to 3% at 100 °C. Response times as low as 3 s were observed when detecting hydrogen at operating temperatures 60–100 °C.

Key words: gas sensing technology, Al-doped ZnO, thin film, ultrasonic spray pyrolysis, gas response.

1. INTRODUCTION

Hydrogen is considered a very promising source of clean energy for transportation, fuel cells, power plants, etc. Due to the wide flammability range of 4–75% for H_2 in air, H_2 storage systems require efficient, fast, and reliable sensors able to function in ambient conditions [1]. Resistance-based semiconductor H_2 gas sensors show potential as inexpensive and portable alternatives to commercially available systems, which are often limited in widespread usage by their large size and high cost [2].

Zinc oxide is an n-type II–VI semiconductor with a wide direct bandgap (3.3 eV) at room temperature, enabling high optical transparency (>80%) in the visible region [3]. It is a suitable semiconductor material for optoelectronic, liquid crystal display, piezoelectric, laser, optical coating, and gas sensing applications [4,5]. This is due to the natural abundance of its component elements and its appealing properties like chemical stability, easily texturable surface, high optical transmittance in the visible and near-infrared ranges alongside low resistivity (10^{-4}–10^{-3} Ωcm) [3,4,6,7].

Several forms of undoped and doped ZnO have been studied for hydrogen gas sensing, e.g. flat or nanostructured thin films, nanowires, nanobelts, and nanotubes [8–12]. In their default state ZnO thin films display long response (t_{res}) and recovery (t_{rec}) times, low sensor response (S), and low selectivity as well as a high optimal operating temperature (T_{op}) exceeding

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200 °C [13]. These properties are commonly used to characterize the performance of semiconductor gas sensors.

In order to improve the gas sensing performance of ZnO, surface modification or doping with other elements is necessary [7]. Undoped and Al-doped ZnO thin films have been prepared by sputtering [1,10], chemical vapour deposition [14], spin coating [15], physical vapour deposition [8], spray pyrolysis [16], etc. Ultrasonic spray pyrolysis is an affordable method that produces smaller droplets than pneumatic spray pyrolysis, yielding a more even coating of the substrate, creating a smoother film surface, and increasing electrical conductivity [17]. Our research group has extensive experience in spray depositing and characterizing undoped and doped ZnO thin films, nanostructures and nano-particles [18–21], but their applicability for gas sensing has not yet been studied. In the literature 5.6% sensor response to 100 ppm H_2 gas was reported in sprayed Al-doped ZnO thin films at 300 °C [13].

The aim of this study was to investigate the H_2 gas sensing capability of Al-doped ZnO (ZnO:Al) thin films deposited by ultrasonic spray at operating temperatures 100 °C and below.

2. MATERIALS AND METHODS

Aluminium-doped zinc oxide (ZnO:Al) thin films were deposited by ultrasonic spray pyrolysis on soda lime glass from a solution containing 0.2 M zinc acetylacetonate (95% w/w $Zn(acac)_2$) and aluminium acetylacetonate (99% w/w $Al(acac)_3$) as dopant. The substrate temperature (T_s) was varied from 280 to 400 °C with ±5 °C accuracy while the Al/Zn ratio in the spray solution was fixed at 5 at% for T_s 280, 320, and 360 °C. Afterwards the deposition temperature was fixed at 400 °C and the Al/Zn ratios 2, 5, 10, 20, or 30 at% were used based on the literature [22]. Henceforth the samples will be referred to as ZnO:Al-#, where # is the Al/Zn molar ratio in the solution. The solvent contained 98% ethanol (96.6% v/v) and 2% acetic acid (99.8% v/v) by volume to prevent formation of zinc hydroxide. The solution spray rate was 2.0 ± 0.3 mL/min and the film growth rate was 20 nm/min. The frequency of the ultrasonic generator was 1.5 MHz.

Phase composition and crystal structure were studied by X-ray diffraction analysis (XRD) on a Rigaku Ultima IV diffractometer (Cu $K_{\alpha 1}$ λ = 1.5406 Å, 40 kV, 40 mA, 2θ 30–70°, step width 0.02°, 10°/min, silicon strip detector D/teX Ultra). Morphology was examined by scanning electron microscopy (SEM, Zeiss Ultra-55) and elemental composition was examined by energy dispersive X-ray spectroscopy (EDS, Bruker Esprit 1.8).

The gas sensing capability measurements of ZnO:Al thin films were conducted in the Microelectronics R&D Laboratory at Northern Illinois University. Two contacts 10 mm apart were deposited onto each sample to ensure sufficient electrical contact with probes. An 8 nm thick Ti binding layer followed by a 200 nm thick gold layer were deposited onto the samples by electron beam evaporation (Temescal BJD-1800). Sensor response to gases was measured as the following ratio [11]:

$$S = \frac{R_{gas} - T_{air}}{R_{air}} \times 100\%, \tag{1}$$

where S is sensor response, R_{air} is the ZnO:Al film resistance in air at the operating temperature, and R_{gas} is the resistance of the film in the studied gas at the operating temperature.

Simplified short-term resistance drift was approximated according to the following equation [23]:

$$Drift = \frac{R_{air,t} - R_{air,0}}{R_{air,0} \times t} \left[\frac{\%}{min} \right], \tag{2}$$

where $R_{air,0}$ is the film resistance in air at the operating temperature prior to the exposure to gas, $R_{air,t}$ is the film resistance in air at the operating temperature at the end of the experiment, and t is the duration of the experiment.

Response time (t_{res}) is the time required for film resistance to reach 90% of the maximum sensor response according to Eq. (1) and recovery time (t_{rec}) is the time required for sensor response to fall from 100% below 10% after gas exposure.

Film resistance was measured by taking ambient air as the base (20.9% O_2, relative humidity 50% at 20 °C) and measuring the resistance change in O_2/99 vol% N_2 and H_2/97 vol% Ar gases at the operating temperatures (T_{op}) 60, 80, and 100 °C ± 0.1 °C by two-point probe analysis (Keithley 4200-SCS). Similar H_2 concentrations (1–2%) have also been used by other groups of researchers [15,24].

The samples were exposed to a steady gas flow for ca 25 s after which the gas flow was immediately shut off and the system was exposed to ambient air for another 25 s while resistance was continuously measured. The samples were left to stabilize for 60 s at the operating temperature before commencing measurements and exposed to ambient conditions for at least one hour after each measurement to restore the ambient adsorption equilibrium.

3. RESULTS AND DISCUSSION

3.1. Structural properties

According to XRD analysis, all deposited ZnO:Al films correspond to hexagonal wurtzite ZnO (reference ICDD 01-075-0576) as its indicative diffraction peaks of (1 0 0), (0 0 2), (1 0 1), 1 0 2), (1 0 3), and (1 1 2) crystallographic planes were detected in the samples (Fig. 1). No phases containing Al were detected by XRD analysis in any ZnO:Al thin films in this study. At higher Al doping levels Al_2O_3 and $ZnAl_2O_4$ may be present in quantities below the detection limit of XRD.

The crystallites in the ZnO:Al-5 films deposited at T_s 280–360 °C are orientated along the (0 0 2) plane parallel to the substrate. The preferred orientation of crystallites in ZnO:Al films deposited at T_s 400 °C changes from (0 0 2) in undoped ZnO and ZnO:Al-2 to (1 0 3) in ZnO:Al-5 and persists at (1 0 1) in ZnO:Al-10-30. The change in the preferred orientation in ZnO films at higher Al doping levels might occur because the ZnO lattice shrinks due to the formation of separate Al–Zn–O or Al–O phases, which limit crystallite growth, or the surface energy of the (0 0 2) plane of ZnO has changed. These phenomena lie outside the scope of this study, but have been commonly observed in spray deposited doped ZnO thin films [4].

The elemental composition analysis of ZnO:Al films deposited at T_s 400 °C indicates that films contain on average half as much Al/Zn as the spray solution (Table 1). Castañeda et al. also noted a deficiency of Al in ZnO:Al films deposited from $Zn(acac)_2$ and $Al(acac)_3$ [25]. The relative deficiency of Al in the films may be caused by evaporation of some portion of Al precursor during deposition [25].
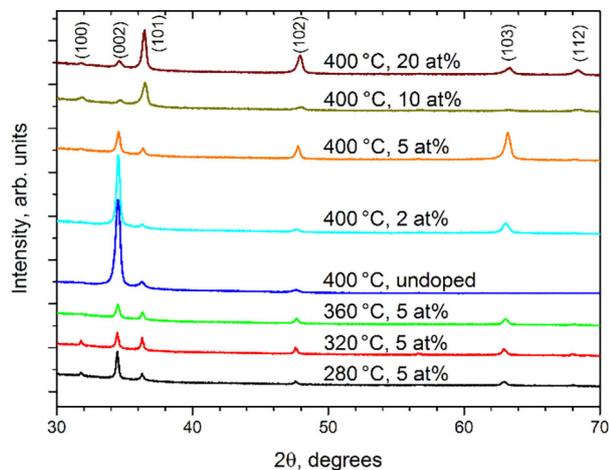
Table 1. Dependence of Al/Zn in ZnO:Al films deposited at T_s 400 °C on Al/Zn in spray solution determined by EDS

Al/Zn in solution, at%/at%	Al/Zn in film, at%/at%
2.0	0.72
5.0	2.4
10	4.3
20	11

3.2. Morphology

The morphology of ZnO:Al thin films deposited at T_s 400 °C was studied. The surface of ZnO:Al-2 consists of hexagonal grains ca. 50–150 nm in size with soft edges (Fig. 2a).

The morphology of the surface of ZnO:Al-5 (Fig. 2b) is visibly different from the hexagonal grains seen in ZnO:Al-2 as grains have become elongated, oval, leaf-like in shape (100–200 nm by 50–150 nm). This is commonly seen in doped ZnO thin films, and also observed in ZnO:In films [21].

The surface of ZnO:Al-10 consists of slightly thinner (50–100 nm) and longer (150–250 nm) grains than those seen in ZnO:Al-5 (Fig. 2c). It is somewhat easier to distinguish the change in the morphology between ZnO:Al-10 and ZnO:Al-20 by the thinner (40–60 nm) and longer (150–300 nm) elongated grains seen on the surface of the latter (Fig. 2d). Columnar stacking of grains and various degrees of agglomeration were seen on the cross-section images (Fig. 3a, b) of the studied ZnO:Al films independent of the doping level.
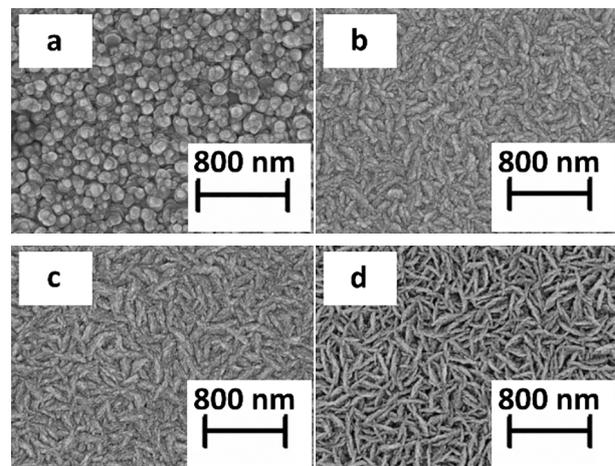

Fig. 1. XRD patterns of ZnO:Al thin films deposited at T_s 280–400 °C. Al/Zn in solution: 0, 2, 5, 10, 20 at%.

Fig. 2. SEM micrographs of ZnO:Al films deposited at T_s 400 °C. (a) ZnO:Al-2, (b) ZnO:Al-5, (c) ZnO:Al-10, (d) ZnO:Al-20.
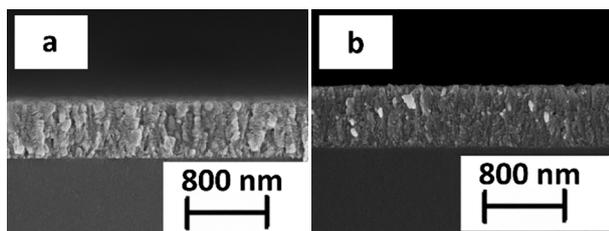
Fig. 3. SEM cross-section micrographs of ZnO:Al films deposited at T_s 400 °C. (a) ZnO:Al-2, (b) ZnO:Al-20.

3.3. Oxygen sensing

The gas sensing mechanism in ZnO:Al thin films is similar to that of ZnO. Atmospheric oxygen adsorbs to the surface of ZnO, depleting the surface of electrons to form O^- species, which increase film resistance [13]. Upon exposure to a reducing gas such as H_2 the adsorbed O^- species on the surface of ZnO react with H_2 and electrons are returned to the surface of the film, resulting in a decrease in film resistance [13].

In order to distinguish the effect of O_2 desorption from H_2 sensing in ZnO:Al films, the response of ZnO:Al films to $O_2/99\%$ N_2 was studied at operating temperatures 60, 80, and 100 °C.

Exposing ZnO:Al-2–ZnO:Al-30 films deposited at T_s 400 °C to 1% oxygen produced a minute response, which decreased with higher Al doping (Table 2). The ZnO:Al-2 thin film as the most resistive ($\sim 1 \times 10^5$ Ω at 100 °C) among the ZnO:Al-2–ZnO:Al-30 films deposited at T_s 400 °C showed the strongest response (0.3–0.7%) and drift (–0.6% to +0.2% min^{-1}), but also the longest response times (11–18 s) at all operating temperatures (Table 2). The ZnO:Al-5 films deposited at T_s 280–360 °C displayed a too significant drift

(–20 to +2% min^{-1}) to provide any accurate and repeatable O_2 sensing results. This is probably due to their much higher resistance at T_{op} 100 °C (7×10^7 Ω, T_s 280 °C; 4×10^6 Ω, T_s 360 °C) (Table 3). For ZnO:Al-5–ZnO:Al-30, $S(O_2)_{60 °C}$ was 0.1–0.3%, $S(O_2)_{80 °C}$ was 0.2–0.7%, and $S(O_2)_{100 °C}$ 0.2–0.6%; t_{res} was 6–15 s and t_{rec} 8–19 s. The drift was negligible at 60–80 °C and from –0.2 to 0% min^{-1} at 100 °C. In conclusion, spray deposited ZnO:Al films were found to be relatively insensitive toward O_2 gas.

3.4. Hydrogen sensing

Exposing ZnO:Al-5 films deposited at T_s 280–360 °C to 3% H_2 yielded $S(H_2)_{60 °C}$ 2.0–2.6% and $S(H_2)_{100 °C}$ 6.1–11% (Table 3). The highest sensor response (11%) was obtained at T_{op} 100 °C with the most resistive ZnO:Al-5 film (7×10^7 Ω) deposited at T_s 280 °C although its recovery times were the longest. The aforementioned films drifted less (–8.6 to +0.1% min^{-1}) in 3% H_2 compared to the exposure to 1 vol% O_2 (–20 to +2% min^{-1}). Response saturation in H_2 was achieved quite rapidly: t_{res} was 3–6 s, t_{rec} 5–11 s. The ZnO:Al-5 film deposited at T_s 400 °C compared to the one deposited at T_s 280 °C, displayed only half the sensor response at T_{op} 100 °C (5.5% vs 11%), but had comparable $S(H_2)_{60 °C}$ (1.6% vs 2.1%), faster t_{rec} (5–7 vs 8–11 s), three orders of magnitude lower resistance (5×10^4 Ω vs 7×10^7 Ω), and up to one order of magnitude smaller drift at T_{op} 60–100 °C. The twice as low sensor response of ZnO:Al-5 deposited at T_s 400 °C is outweighed by nearly tenfold increased stability. Hence, 400 °C was determined as the optimal deposition temperature for ZnO:Al films and chosen for studying the effect of Al doping on H_2 gas sensing.

Table 2. Sensing properties of ZnO:Al-2–ZnO:Al-10 films deposited at T_s 400 °C to $O_2/99\%$ N_2

Al/Zn, at%	T_{op}, 60 °C					T_{op}, 100 °C				
	S, %	Drift, % min^{-1}	R_{air}, Ω	t_{res}, s	t_{rec}, s	S, %	Drift, % min^{-1}	R_{air}, Ω	t_{res}, s	t_{rec}, s
2	0.31	0.24	1.3E5	18	–	0.64	–0.62	1.1E5	11	14
5	0.17	0.04	5.0E4	8	12	0.57	–0.20	4.2E4	7	13
10	0.11	–0.02	6.8E3	13	15	0.36	–0.06	6.2E3	8	12

Table 3. Sensing properties of ZnO:Al-5 films deposited at T_s 280–400 °C exposed to $H_2/97\%$ Ar

T_s, °C	T_{op}, 60 °C					T_{op}, 100 °C				
	S, %	Drift, % min^{-1}	R_{air}, Ω	t_{res}, s	t_{rec}, s	S, %	Drift, % min^{-1}	R_{air}, Ω	t_{res}, s	t_{rec}, s
280	2.0	–0.57	1.2E8	5	8	11	–4.0	7.2E7	3	11
320	2.1	–1.1	1.5E7	3	6	6.1	–4.4	6.2E6	3	7
360	2.6	–3.5	1.1E7	3	6	8.8	–8.6	3.6E6	3	7
400	1.6	–0.12	5.2E4	4	5	5.5	–0.38	4.4E4	3	7

Table 4. Sensing properties of ZnO:Al-2–ZnO:Al-30 films deposited at T_s 400 °C exposed to H_2/97% Ar

Al/Zn, at%	T_{op}, 60 °C					T_{op}, 100 °C				
	S, %	Drift, % min^{-1}	R_{air}, Ω	t_{res}, s	t_{rec}, s	S, %	Drift, % min^{-1}	R_{air}, Ω	t_{res}, s	t_{rec}, s
2	3.1	0.04	1.4E5	3	6	7.9	−0.95	1.2E5	3	7
5	1.6	−0.12	5.2E4	4	5	5.5	−0.38	4.4E4	3	7
10	0.83	−0.21	6.8E3	4	4	3.4	−0.28	6.2E3	5	6
30	0.70	−0.15	4.0E3	6	8	2.6	−0.23	3.7E3	5	5

Sensor response increased in all films deposited at T_s 400 °C as the operating temperature was raised from 60 to 100 °C (Table 4). This could be caused by more complete water evaporation from the film surface, increasing the available surface area for hydrogen adsorption [1]. At every T_{op} ZnO:Al-2 outperformed the 100 times less resistive ZnO:Al-10, ZnO:Al-20, and ZnO:Al-30 in H_2 sensing by about twofold (Fig. 4). The sensor response to H_2 and drift decreased at higher deposition temperature and higher Al doping as resistance decreased (Table 3, Table 4).

Response times were only 1–3 s longer at every operating temperature for ZnO:Al-5–ZnO:Al-30 compared to 3 s for ZnO:Al-2. In comparison, the response time to 1000 ppm H_2 gas was 10 min at 100 °C for sputtered ZnO:Al films studied by Galstyan et al. [26]. The recovery time was on average 6–7 s at 60–100 °C (Table 4) longer than the response time.

The ~10% sensor response to H_2 at 100 °C obtained in this study is similar to what other groups have achieved with spray deposited ZnO:Al thin films, although deposition and sensing parameters differed [13,27]. Prajapati et al. [13] achieved 5.6% sensor response to 100 ppm H_2 at T_{op} 300 °C with 300–400 nm thick

ZnO:Al films sprayed at T_s 410 ± 10 °C, 1 at% Al/Zn in the solution. Drift, response, and recovery times were unfortunately not studied by Prajapati et al.

The relatively fast response (<6 s) and recovery times (<10 s) achieved in this study are comparable with the fastest response times achieved with resistance-based thin film hydrogen sensors in the literature and substantially faster than most reported ZnO thin films: 2 s response time for spray deposited SnO_2 thin films operating at 350 °C and 1000 ppm H_2 [1], 58 s for ZnO thin films deposited by metalorganic chemical vapour deposition operating at 300 °C and 200 ppm H_2 [14].

Our Al-doped ZnO thin films did not undergo post-deposition treatment; thereby we lowered production costs. The relatively low observed sensor response in our films may be due to surface contamination during storage, which limits the sensor response of ZnO:Al thin film gas sensors. In our earlier studies it was determined that storage conditions and ageing have a substantial effect on the surface chemical composition and consequently the surface wettability and photocatalytic activity of spray deposited ZnO thin films [20].

If we applied post-deposition heat or UV treatment to the films to decontaminate the surface layer before measuring gas sensing properties, as has been done in numerous studies [1,3,8], even better gas sensing properties could be expected. Therefore, it is necessary to pursue affordable surface modification alongside doping to ensure long-term protective and catalytic coatings to raise the H_2 sensing efficiency of spray deposited ZnO:Al thin films.

4. CONCLUSIONS

Spray deposited Al-doped ZnO thin films are sensitive toward 3% hydrogen ($S \sim 8\%$), but insensitive toward oxygen ($S < 0.7\%$). The H_2 gas sensing response times of the ZnO:Al film to 3% H_2 are as low as 3 s and recovery times as low as 5 s. As expected, sensor response to H_2 increased as the operating temperature was raised from 60 to 100 °C.

To conclude, T_s 400 °C yielded ZnO:Al films with the most stable and repeatable H_2 response despite the
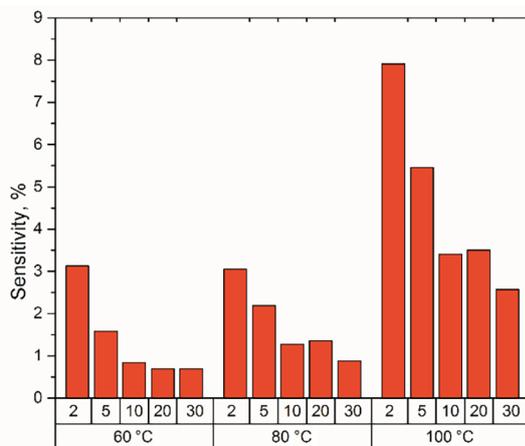

Fig. 4. Effect of aluminium doping on the H_2 sensor response of ZnO:Al films deposited at T_s 400 °C at operating temperatures 60, 80, and 100 °C. Al/Zn in solution: 2, 5, 10, 20, 30 at%.

somewhat reduced sensor response. Aluminium doping had a beneficial effect on reducing drift, but sensor response diminished in films sprayed with Al content higher than 2–5 at% Al/Zn in the solution due to decreased film resistance.

Therefore, ultrasonically spray deposited Al-doped ZnO is suitable for application at working temperatures lower than 100 °C in real working conditions. However, sensor response could be improved further by optimizing deposition parameters and exploring surface modification and texturization in addition to Al doping. We suggest that further studies combining surface modification and doping to preserve the long-term sensor response of ZnO:Al films be carried out.

ACKNOWLEDGEMENTS

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Pihustussadestatud alumiiniumiga legeeritud ZnO õhukeste kilede gaasitundlikkus

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Alumiiniumiga legeeritud tsinkoksiidi õhukesed kiled sadestati tsinkatsetüülatsetonaadist ja alumiiniumatsetüülatsetonaadist erinevatel alumiiniumi kontsentratsioonidel töölahuses ning erinevatel sadestustemperatuuridel ultraheli-pihustusmeetodil. Struktuuri, morfoloogiat ja elementkoostist uuriti vastavalt röntgendifraktsioonanalüüsi, skaneeriva elektronmikroskoopia ning energiadispersse röntgenspektroskoopia meetodil. Gaasitundlikkust uuriti kahe sondi meetodil O_2/99% N_2 ja H_2/97% Ar gaasides töötemperatuuril 60, 80 ning 100 °C. Kiled koosnevad heksagonaalse vürtsiidi vormis tsinkoksiidist. Kilede pinnamorfoloogia sõltub alumiiniumi legeerimismäärast. Alumiiniumiga legeeritud tsinkoksiidi õhukeste kilede tundlikkus vesiniku suhtes väheneb sadestustemperatuuri tõstmisel 280–400 °C 11 protsendilt 5,5 protsendile, kuid stabiilsus paraneb suurusjärgu võrra. Kiledest, mis sadestati substraadi temperatuuril 400 °C, osutus 2 aatomprotsenti Al/Zn sisaldavast lahusest sadestatud kile 3 mahuprotsendi H_2 detekteerimisel kõige tundlikumaks, reageerides 8% takistuse muuduga. Lisades pihustatavasse lahusesse enam kui 2 aatomprotsenti Al/Zn, suureneb kilede juhtivus kahe suurusjärgu võrra ja tundlikkus kahaneb kuni 3% töötemperatuuril 100 °C. Töötemperatuuril 60–100 °C täheldati vesiniku detekteerimisel reaktsiooniaegu, millest lühimad olid 3 sekundit.