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Chapter

A Review on Preparation of ZnO Nanorods and Their Use in Ethanol Vapors Sensing

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Abstract

The devices of polycrystalline film have small sensitivity that can be overthrown by using high aspect ratio of 1D nanostructures, such as ZnO nanostructures. Sensors based on 1D nanostructures show very quick response time and high sensitivity for their high impact factor. The purpose of this article is to provide a comparison of different methods and the quality of the sensors thus produced. Currently, metal oxide 1D nanoarchitectures like ZnO have great attraction due to their applications in sensors. Metal oxide nanostructures have high aspect ratio, with small consumption of power and low weight, however, keeping excellent chemical and thermal dependability. Different techniques have been adopted to fabricate metal oxide one-dimensional nanostructures like hydrothermal, electro-spinning, sol-gel, ultrasonic irradiation, anodization, solid state chemical reaction, molten-salt, thermal evaporation, carbothermal reduction, aerosol, vapor-phase transport, chemical vapor deposition, RF sputtering, gas-phase-assisted nanocarving, molecular beam epitaxy, dry plasma etching, and UV lithography. The sensitivity depends upon the materials; synthesis technique and morphology of the sensor performance toward a particular gas have different range of success. This article estimates the efficiency of ZnO 1D nanoarchitectures, gas sensors. Finally, in this review, we had mentioned the future directions of investigations in this field.

Keywords: ethanol, gas sensing, epitaxy, anodization, ZnO, nanostructures

1. Introduction

The semiconductor metal oxides play the role of an encouraging contester for gas sensing employment. As a result, they have greater sensitivity for target gases due to easy synthesis techniques, being cheaper, and great compatibility with other techniques [1]. Nowadays, nanoarchitectures are being designed from SnO_2, In_2O_3, ZnO, WO_3, TiO_2, CdO, TeO_2, MoO_3, CuO, and Fe_2O_3 with various dimensions and configurations. It was explored that surface morphology plays an important role in sensing applications [2, 3]. Semiconductor metal oxide nanostructures have various compositions and morphologies such as single crystals, one dimensional, and thin or thick film form due to utilization of interest and facility of synthesis techniques [4]. Recently, 1D nanoarchitectors have much attraction

for sensing due to their aspect ratio beside their thermal and chemical stabilities at various working situations [5, 6].

In nanotechnology and nanoscience, advancement in synthesis techniques for manufacturing 1D nanostructures has been an important target [7]. Various techniques have been adopted to fabricate 1D nanostructures for gas detection applications. These fabrication methods are sol-gel [7], ultrasonic irradiation [8], solid-state chemical reaction [9], electrospinning [10], molecular beam epitaxy [11], hydrothermal [12], thermal evaporation [13], molten-salt [14], anodization [15], RF sputtering [16], vapor-phase transport [17] chemical vapor deposition [18], carbothermal reduction [19], nanocarving [20], dry plasma etching [21], aerosol [22], and UV lithography. Various kinds of nanostructures can be fabricated with different morphologies that are directed by fabricating techniques and treatments.

Nanostructures grown by these techniques contain the shape of nanowires [19], nanobelts [16], nanotubes [15], nanoneedles [23], nanorods [5], nanofibers [12], nanoribbons [24], nanowhiskers [25], urchins [26], nanopushpins [27], fiber-mats [22], hierarchical dendrites [17], nanocarving [20], and lamellar [28]. The modifications in surface morphology result in sensing of various kinds of oxidizing and reducing gases like CO, NH_3, NO_2, H_2, O_2, H_2S, LPG, xylene, propane, toluene, triethylamine, methanol, and acetone.

The sensitivity of a one-dimensional nanostructure sensor can increase with the improvement in surface morphology and bulk characteristics. These improvements can be made by doping with other elements or decorating nanoparticles on the surface of nanostructures. Sensors using such kinds of surface morphology and bulk characteristic improvements indicate significantly greater response as compared to that of unrestricted sensors.

The current article shows a detailed discussion of the contemporary investigation of the vigorous developments and adopting techniques for designing 1D SMO sensors. The sensor synthesize with nanostructures shows high sensitivity. This article's exemplary supposition investigates the 1D ZnO nanostructure sensor for ethanol detection process. Finally, conclusions explain the possible future evolution in 1D zinc oxide nanostructures for ethanol sensing.

2. Synthesis of ZnO nanostructures

The growth of ZnO nanostructures can be categories as follows: (a) wet chemical method, (b) solid-state synthesis, and (c) vapor-phase process. Wet chemical process consists of hydrothermal and ultrasonic irradiation growth in solution. However, ZnO nanostructures can be fabricated by solid-state route either through the solid-state chemical reaction or through the carbothermal reduction. The chemical vapor deposition process, molecular beam epitaxy (MBE), thermal evaporation, RF sputtering, vapor-phase transport, and aerosol are included in vapor-phase route. The processing particulars for synthesis of ZnO 1D nanostructure are illustrated in **Table 1**.

2.1 Wet chemical process for the growth of one-dimensional nanostructures

2.1.1 Hydrothermal process

Liwei Wang has synthesized ZnO NRs with hydrothermal technique in greater quantity (about 85%), in $Zn(OH)_4^{2-}$ solution and the presence of cetyltrimethylammonium bromide. CTAB act as a structure director, in the absence of any calcination technique [29].

Processing route	Synthesis technique	Starting material	Synthesis temperature (°C)	Morphology	Diameter of ZnO nanostructure	Length of ZnO nanostructure	Reference
Wet process route	Low-temperature process in autoclave	$(Zn(NO_3)_2 \cdot 6H_2O)$, NaOH, CTAB	90°C for 15 h	ZnO nanorods	90–200 nm	1.7–2.1 µm	[29]
	Hydrothermal process	CuO co-doped ZnO	Room tem.	CuO-ZnO NRs			[30]
	Hydrothermal	$ZnCl_2$ in NH_4OH	400 for 3 h	ZnO capsules			[31]
	Wet chemical technique	$Ag/Ag_2O_3/ZnO$ NRs	Low tem. NRs	300 nm NRs	300 nm		[32]
	Wet chemical low-temperature process	1.0239 g $ZnCl_2$ (7.50 mmol), 3.006 g NaOH (75.00 mmol), 25 mL deionized water	90°C 3 h, 80°C for 12 h °C	Flower-like ZnO nanorods	200–500 nm	1.0–1.5 µm	[32]
	Two-step solution growth	$ZnCO_3$, CO_2-ethanol, KOH		ZnO NRs	150 nm	4 µm	[33]
	Solution growth technique Hydrothermal technique	$LiNbO_3$ Zinc nitrate, hexamethylenetriamine, and polyethylenimine in deionized water	95°C 80°C for 12 h	Nanorods	45 nm	1 µm	[34]
		$ZnAc_2 \cdot 2H_2O$, poly(ethylene glycol) 3 g of NaOH	120°C for 12 h. Dried 60°C for 4 h	Ag-ZnO NRs, nigger-brown	—	—	[31]
		$Zn(NO_3)_2.6H_2O$ $C_6H_{12}N_4$	80°C	Nanorods	30–50 nm	1.2 µm	[35]
		10 ml $Zn(Ac)_2.2H_2O$ in 0.1 M methanol, 20 ml NaOH in 0.5 M methanol, DI water ($K_2SnO_3 \cdot 3H_2O$, 95%), 0.75 g of urea	150°C for 24 h for ZnO NRs and for $ZnSnO_3$ 3 h at 170°C	ZnO NRs	2.8 nm, 2.5 nm	26 and 22 nm	[36]
		$Zn(NO_3)_2 \cdot 6H_2O$ $C_6H_{12}N_4$	80°C deposition time was 16 h	ZnO NRs	30–50 nm	—	[37]
		20 mM $Zn(NO_3)_2$ 20 mM hexamethylenetetramine	90°C for 100 min, dried for 12 h at 60°C and annealed 1 h at 500°C	Well-dispersed ZnO nanorods	290–330 nm	3.2–3.4 µm	[38]

Processing route	Synthesis technique	Starting material	Synthesis temperature (°C)	Morphology	Diameter of ZnO nanostructure	Length of ZnO nanostructure	Reference
	Sol-gel	$Zn(CH_3COO)_2 \cdot 2H_2O$	95°C 50 ml autoclave	Nanorods	51 and 33 nm	262, 748, and 470nm	[39]
		$Zn(CH_3COO)_2$, $2H_2O$ 2-propanol $C_4H_{11}NO_2$, zinc acetate dehydrate, $(CH_2)_6N_4$	75°C for 30 min	Hexagonal NRs	60–70 nm	-	[40]
	One-step solvothermal method	20 mM $Zn(NO_3)_2$ and 20 mM HMTA	90°C for 100 min	Nanorods	220 nm	—	[41]
	Hydrothermal synthesis	$Zn(NO_3)_2.6H_2O$ sodium hydroxide deionized water CTAB	120°C for 12h	ZnO nanorods	80–150 nm	—	[42]
	Ultrasonic irradiation in aqueous solution	Alumina substrate, $Zn(NO_3)_2 \cdot 6H_2O$, $(CH_2)_6N_4$	—	Nanorod (vertically aligned)	50 nm	500 nm	[11]
	DC magnetron sputtering	ZnO (0, 1, 10, and 25 at. wt%) ZnO, MoO_3, Au-IDE, acetone	Annealing in ambient air for 1 h at 773 K	Nanostructures	—	—	[43]
		Metallic zinc foil and formamide solution	55°C	Hexagonal-shaped ZnO nanorods	400 nm	2 μm	[44]
		ITO glass, 7 Ω/sq., CBD (CBD condition: 95°C, 3 h),170 nm thick seed layer	400°C for 1 h	ZnO nanorods	55 nm	1.5 μm	[45]
	Solution method	$Zn(NO_3)$ $6H_2O$ (10 mM), $(C_6H_{12}N_4,$10 mM), $CoSO_4 \cdot 7H_2O$, 0–0.5 mM	90°C for 15–30 min	ZnO nanorods	100–300 nm	1–3 μm	[46]
		$Zn(NO_3)_2(H_2O)_6$, NH_3	80°C for 3 h	ZnO nanocrystals	—	—	[47]
	Microwave irradiation	Zinc acetate dihydrate, NaOH	Dried at 60°C Calcined 600°C, 2 h	ZnO flower-like	200–300 nm	1.5 μm	[48]
		$(CH_3COOH)_2 \cdot 2H_2O$, HMTA, CTAB	120°C for 12 h in autoclave	Hexagonal ZnO nanosheets	17 nm	90 nm	[49]

Processing route	Synthesis technique	Starting material	Synthesis temperature (°C)	Morphology	Diameter of ZnO nanostructure	Length of ZnO nanostructure	Reference
	Seeding by RF-sputtering, thermolysis-assisted aqu. sol. tech.	0.01 mol $C_6H_{12}N_4$, in 400 ml DI water	85°C	ZnO nanorods	8–160 nm thick seed layer	—	[30]
	Solvothermal	$Zn(CH_3COO)_2 \cdot 2H_2O$, methanol, KOH	70°C. 3–5 days	NRs	15 nm	50–120 nm	[50]
Solid-state technique							
Vapor-phase technique	Carbothermal reduction	0.3 g Zn powder and 0.6 g active carbon	900°C at a rate of 25°C/min for 2 h	Nest-like ZnO	—	—	[51]
	Continuous two-step vapor growth	$(CH_3)_4Sn$, DI water, IPA, PDMS substrate	900°C	NWs	50–80 nm thick	Several micrometers	[52]
		ZnO powder	600°C	NRs	Average diameter 400 nm, 550 nm	11.8 μm, 6.5, and 3.5 μm	[53]

Table 1.
Details of different growth techniques of ZnO 1D nanoarchitectures.

Semiconductor metal-doped transition nanomaterials have a number of applications. The hydrothermal growth technique is cost-effective and environment-friendly. The nanostructures of CuO doped with ZnO synthesized at room temperature by hydrothermal technique need great efforts. The properties of CuO doped with ZnO nanorods were measured by various spectroscopy techniques, and sensing was executed by I-V analysis. Aqueous ammonia was used as analytic gas as reported by M. Rahman et al. CuO nanorods doped with ZnO sensor show good stability, sensitivity, and reproducibility. Sensor based on signal/noise ratio has sensitivity of 1.549 ± 0.10 μA cm^{-2} Mm^{-1}. Sensor applications depend on the transition metal coated with ZnO nanomaterial [30].

ZnO nanoparticles were synthesized hydrothermally from urea and zinc chloride and characterized by various spectroscopic techniques. The ZnO NPs range in size from 180 to 130 nm with hexagonal structure. The photocatalyst analysis of ZnO nanoparticles was determined with the degradation of methylene blue. ZnO nanostructures were possessed by high photocatalyst value as compared to TiO_2-UV100. Moreover, the sensing characteristics of the detector were determined with methanol by I-V process at room temperature. It was investigated that sensor shows sensitivity in the range of 0.9554 μA cm^{-2} mM^{-1} at room temperature [39].

ZnO nanocapsules have been synthesized hydrothermally. The structural morphology and characteristics were analyzed with the help of different spectroscopy techniques. The sensing was measured with I-V method by using chloroform as the detecting gas. Sensor shows high sensitivity, small detection limit, and high linear dynamic limit with fine linearity in a small response time. Moreover, the photocatalytic response was calculated with the degradation of acridine orange [31].

Nanoparticles of ZnO-CeO$_2$ were grown by hydrothermal process. These nanostructures were used for the construction of sensor and photocatalyst by elimination of environmental pollution. These NOs have diameter approximately from 50 ± 10 nm. The composition of NPs was measured by EDS spectroscopy, and UV-visible spectrum investigates the optical characteristics. The photocatalytic degradation of acridine orange and methylene blue dyes has been carried out using ZnO-CeO$_2$ NPs. The critical routine of ZnO-CeO$_2$ NPs for ethanol detector shows high sensitivity and small detection limit in shorter time [46].

The nanostructures of ZnO-CeO$_2$ were grown by hydrothermal technique. These nanostructures have extended shaped CeO$_2$ NPs having diameters of 40–90 nm. Photocatalytic activity of CeO$_2$ co-doped ZnO structure was measured with degradation of acridine orange and methylene blue. Sensor fabricated by ZnO-CeO$_2$ nanostructures shows high sensitivity in 10 s. The chemical sensor used ethanol as the sensing gas using I-V procedure [50].

ZnO NR sensor for ammonia detection has been synthesized by wet chemical technique at cost-effective low temperature. The as-synthesized sensor exhibited high sensitivity of 5.538 mA cm^{-2} mM^{-1}, in small detection range of 0.11 mM, with linear-dynamic limit from 0.5 mM, having high linearity of 0.7102 in 10.0 s response time. In addition, sensor performs good for the degradation of acridine-orange, methylene-blue, and amido black. Spectroscopy analysis exhibited that ZnO NRs have wurtzite crystalline structure with diameter of 58.61 nm [50].

The calcined AgO co-doped ZnO NPs were synthesized by hydrothermal process using alkaline medium as reducing agent. The as-prepared NPs were analyzed by different spectroscopy techniques. Sensor was fabricated on a microchip for methanol sensing that exhibited high response. Careful observation exhibits that microchip sensors have high value of sensitivity, reliability, small volume reproducibility with ease of integration, high stability, and good response. The calibration graph is linear over methanol concentration. The sensitivity was measured at 3 at signal-to-

noise ratio having the value of 7.917 Ma cm^{-2} mmol L^{-2} with a detection range of 71 $\pm$ 0.5 µmol L^{-1} [45].

A reliable technique for detecting dissolved acetone by doped nanomaterials was investigated by Mohammed M. Rahman et al. ZnO NRs co-doped with Co$_3$O$_4$ were fabricated by solvothermal process. The as-fabricated NRs were characterized for different spectroscopic techniques. NRs were calcined at 400°C that shows excellent semiconductor nanomaterial for sensing acetone with silver electrodes. The detector exhibits high sensitivity, reproducibility, and stability. The calibration graph is linear and exhibits high sensitivity and small detection range in large concentration of acetone [40].

Here, we investigate hydrothermal growth of Ag/Ag$_2$O$_3$/ZnO NRs that exhibit high crystalline structure. The characterization confirms that composite NRs have 300 nm cross-section areas. The composite NRs have absorption edge at 375 nm that exhibited that they are optically active. The sensor shows high sensitivity and small detection range. Hence, NRs can be used as redox mediator for efficient phenyl-hydrazine detector [33].

Good-quality crystalline ZnO NPs were prepared by hydrothermal process using aqueous solution of zinc chloride and ammonium hydroxide. Nanoparticles have wurtzite geometry with an approximate size of 50 $\pm$ 60 nm. The composition quality of the as-prepared NPs exhibited 1:1 stoichiometry of Zn and O$_2$, which was confirmed from spectroscopy analysis. The optical characterization of ZnO NPs exhibits that they are used as photocatalyst for the degradation of acridine-orange and for the detection of acetone. The constructed sensor shows high sensitivity of 0.14065 µA cm^{-2} mM^{-1} and small detection range in 10 s [32].

ZnO NRs in vertical direction were synthesized on flexible polyimide films by a thermolysis-assisted chemical solution method [42].

ZnO nanorod arrays with various aspect ratios and characteristics relevant to tailored defect are prepared and used to synthesize gas sensors. The ZnO gas sensors are of three different types synthesized by sol-gel process and successive aqueous chemical growth (ACG). According to Shi et al. and Vayssieres et al., ACG solutions used in the current research work are two types: Zn salt/KOH and Zn salt/HMTA [41].

An accomplished photochemical method was used for the synthesis of Ag NPs decorated on ZnO nanorods for investigation of gas sensing. ZnO NRs decorated with Ag increased long-term stability and response time [54].

NRs with and without Co doping were synthesized in 10 mM solution of zinc nitrate hexahydrate Zn(NO$_3$)·6H$_2$O, hexamethylenetetramine, and 0.5 mM cobalt sulfate hydrate (CoSO$_4$·7H$_2$O) in water at 90°C for 15–30 min. The sensor showed high response and sensitivity as NRs fabricated by electrodeposition process [44].

To fabricate ZnO nanorods by solvothermal technique, prepare a 1.12 M solution of zinc acetate dihydrate in methanol (40 mL) under vigorous stirring at 70°C. Particularly, at 70°C, add 21.33 mL solution of KOH (21.33 mL) dropwise in methanol. After 2 h of vigorous stirring of the mixture, transfer it to 100 mL autoclaves, which were allowed to react at 70°C for 3–5 days and then cooled down naturally. Harvest the resultant product [35].

1D ZnO NRs were grown on ITO-coated glass (AUO Co., Ltd.). The ITO glass has 7 Ω/sq. resistance in sequential chemical bath deposition. A seeding layer was deposited with a thickness of 170 nm at 25°C by the process of dip coating in the first step and then followed by the process of CBD at 95°C for 3 h with the synthesis of ZnO nanorods in 0.05 M precursor solution of ZnO. The ZnO samples were thermally treated at 400°C for 1 h in an electric furnace after deposition. Ethanol of analytical grade and deionized water with 2.61 µs/cm and pH 6.7 were used in the experiment [49].

ZnO nanorods were prepared from HMT solution on p-Si substrate using oxidation furnace at 1000°C for drying 30 min following 2 h wet oxidation process. The seed layer for ZnO nanocrystal was prepared with zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) in 2-propanol by sol-gel process. Then, 3 ml diethanolamine ($C_4H_{11}NO_2$) was added dropwise to clear the solution and aged for 24 h. The samples were spin coated and annealed at 450°C for 1 h. A 50 ml solution in deionized water (~18.2 MΩ cm) of zinc acetate dihydrate and $(CH_2)_6N_4$ in 1:3 mass ratio was prepared. Then, the substrate was placed into the nucleation solution at 75°C for 30 min [36].

ZnO NRs were fabricated from $ZnCO_3$ fibers that were formed in a solution of CO_2-ethanol, by consecutive treatment in KOH solution. The ZnO NRs were single crystal with a diameter of 150 nm and length of 4 μm. It was observed that ethanol sensing was done at 250°C [48].

ZnO nanorods having a flower-like shape were fabricated at 90°C by the hydrothermal process in the absence of any surfactant, organic solvent, or toxic regent. In a particular growth, solution A was formed by dissolving 7.50 mmol $ZnCl_2$ in 25 mL deionized water under stirring. Adopting the similar technique, 75.00 mmol NaOH was dissolved in 25 ml deionized water consequence in solution B. Finally, solution A was added into B dropwise under stirring. The resultant solution was placed at 90°C for 3 h, harvesting the white precipitate rinsed with deionized water and drying them in vacuum for 12 h at 80°C [38].

ZnO nanorods were fabricated by dissolving 2.97 g $Zn(NO_3)_2 \cdot 6H_2O$ and 4.00 g NaOH (molar ratio of Zn^{2+}/OH^- by1:10) in 200 ml DI water. Consequently, 5.00 g CTAB was added under vigorous stirring for 1 h. The solution was shifted to a Teflon-lined steel autoclave and kept at 120°C for 12 h and then allowed to cool down naturally. Then, white precipitates were collected, washed, and dried overnight at 60°C. At a pressure of 6.0 MPa, ZnO NRs were used to design a sensor. The pellets were 3.0 mm thick and have an area of 5.3 cm^2. On the surface of pellets, electrodes of 2.0 cm^2 were deposited by silver paste [47].

A 20 mM nutrient solution of $Zn(NO_3)_2$ and hexamethylenetetramine (HMTA) was prepared. The used precursors are such a kind that dissolved in necessary solvents. After dissolving $Zn(NO_3)_2$ and HMTA precursor solutions, the beaker was covered. Then, it was put in an oven for 100 min at 90°C. After cooling down naturally, the white precipitates were collected by centrifuging and rinsed and dried at 60°C for 12 h. Calcinations were done for 1 h at 500°C in the presence of air. The samples prepared with 0, 10, 20, 30, 40, and 50 vol% ethanol solvent were numbered a0, a10, a20, a30, a40, and a50, respectively [55].

To fabricate one-dimensional multifaceted ZnO nanostructures, a new strategy has been introduced that consists of two-phase solution process. Through these techniques, nanowires, nanorod arrays (NAs), nanotubes, nanorod hollow spheres (NHSs), nanoribbons, and nanonetworks were grown at low temperature without any catalysts, templates, or precursors [53].

ZnO nanostructures with different morphologies have been grown from zinc foil (1×1 cm^2) and substrates were cleaned by ultrasonication process in ethanol. The substrates were suspended vertically to the bottom of a vial in formamide solution 3 ml of 15%. The vial with substrate was sealed and put inside an oven with fixed temperature at 55°C. The samples were washed thoroughly with ethanol and dried. Time-dependent experiments estimate the illumination transformation process as well as reaction time of ZnO nanodisks from NRs [43].

Filtered cathodic vacuum arc (FCVA) mechanism was introduced to deposit ZnO layer on the surface of alumina substrates decorated with gold IDTs. The substrates were loaded in the holder with varied temperature heater. After completion of deposition, the substrate was carried out for analysis from the chamber.

The ZnO seeding layer will act as nucleation site for the fabrication of ZnO NRs from hydrothermal process. An equimolar growth solution of zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and $C_6H_{12}N_4$ was prepared. The transducers were washed ultrasonically in acetone and dried in nitrogen atmosphere. Then, the transducer was kept inverted on Teflon holder and attached to a glass rod before inserting into the reaction bottle. The bottle was placed in an oven for 16 h at 80°C. Finally, the substrate was washed thoroughly to remove impurities and dried in N_2 stream at a flow of 200 sccm [51].

A solution of 1 mM zinc acetate dihydrate ($Zn(CH_3COOH)_2·2H_2O$), 0.5 mM hexamethylenetetramine, and 0.05 g cetyltrimethylammonium bromide (CTAB) in 40 mL deionized water was prepared after vigorously stirring for 1 h. Then, the mixture was transferred in autoclave and placed under heat treatment for 12 h at 120°C. After centrifugation, the white precipitates were harvested, rinsed with ethanol and deionized water. Finally, the product was dried in air atmosphere at 60°C [52].

2.2 Sol-gel process

2.2.1 Preparation of seed layer and ZnO nanorod arrays

The ZnO nanorod array was fabricated by dissolving 10 ml $Zn(Ac)_2·2H_2O$ in 0.1 M methanol and 20 ml NaOH in 0.5 M methanol solution. After filtration, the solution was transferred to a 50 ml autoclave and heat treated for 24 h at 150°C. The precipitates were collected and washed. For hydrothermal growth of $ZnSnO_3$ nanorods, 0.06 g of ZnO nanorods was dissolved by ultrasonication (Power, 500 mW) in 32 ml of water-alcohol (38 vol% alcohol) mixture. Then, 0.115 g of potassium stannate trihydrate ($K_2SnO_3·3H_2O$, 95%) and 0.75 g of urea were transferred to the above mixture. After vigorous stirring for 5–10 min, the solvent was shifted into a 50 ml autoclave and heated for 3 h at 170°C. A white product was obtained and rinsed with distilled water [34].

2.3 Solid-state processing route (microwave irradiation)

A 0.1 M solution of zinc acetate dehydrates was prepared and vigorously stirred for 10 min. To obtain 0, 2, 5, and 10 wt% samaria, a suitable quantity of samarium nitrate was added during magnetically stirring. Then, guanidinium carbonate (0.1 M) solution was dropped to the mixture. Consequently, 10 min latter, 4 M solution of NaOH also was added dropwise to attain a clear solution with pH 12. Lastly, the microwave irradiation (with 75% power) was exposed to the mixture for 2 min. For irradiation, a microwave oven was used with a power of 800 W (Concave Reflex Systems (C.R.S.), KOR-63A5). The white precipitates were separated, rinsed, dried under vacuum at 60°C, and calcined for 2 h at 600°C in air [56].

Interdigital electrodes (IDTs) were placed on the upper surface of alumina substrate (96%), with line/space of 30 μm. Actually, such kind of line-printing is not feasible with thick film method. By a laser printer of gold film, the interdigital electrodes were printed [57].

A 20 mM nutrient solution (equal molar solution) of $Zn(NO_3)_2$ and HMTA in distilled water was prepared, and 4:1 volume ratio of the anhydrous ethanol was added. Precursors were formulated by dispersing in their relative solvents. The container with precursors was put in an oven for 100 min at 90°C. After cooling, the white sludge was collected and cleaned using centrifuge and rinsing water. Finally, the sludge was dried for 12 h at 60°C and annealed in air for 1 h at 500°C [58].

2.4 Vapor-phase route (pulsed laser deposition)

ZnO nanorods were grown onto the long-period gratings (LPGs), followed by a two-step process. They contain pulsed laser deposition (Zn layer onto optical fiber), followed by the growth of ZnO nanostructures in aqueous solution. Zinc precursor layer was deposited by a laser beam (248 nm KrF excimer) that was focused on target (Zn target with 99.9% purity) to produce fluence (1.3 J/cm^2). The evaporated material was deposited on the optical fibers located at 6 cm apart from the target. According to identical conditions, the deposition on substrate has resulted in Zn layer nearly 40 mm thick, when exposed with 2000 laser pulses [59].

2.5 RF sputtering

A seeding of ZnO was sputtered (5 nm) on the recommended area of CMOS devices and illustrated with metal shadow mask. The as-prepared substrate was dipped in 25 mM equimolar solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine and was maintained for 2 h at 90°C. The device was removed from the nutrient solution after ZnO NWs' growth washed with deionized water and dried. This process is suitable for simultaneously growing ZnO NWs on microhotplate and provides an economic process for thin film level growth as well [60].

By RF sputtering process, deposit a layer of 50 nm on the glass substrate. Wash the substrate with standard process and keep the substrate in its holder. The NRs of ZnO:Ti were grown onto the ZnO sputtered by reactive evaporation with hot-wire resistance in a furnace. After the growth of ZnO:Ti NRs, the Pt electrodes were deposited by photolithography and liftoff technique on the substrate. For better ohmic contact, anneal the samples in an Ar ambient atmosphere for 15 min at 350°C [61].

Prepare nanostructured thin film with pure ZnO (25 at. wt%) and MoO_3 for gas response. Deposit it on the surface of as-prepared alumina sensor chips by sputtering and annealing process. The sensor chips containing Au-IDE and thin film Pt-heater structures were comprehended by means of DC magnetron sputtering, plasma etching, and UV-lithography. Gold wires (diameter of 50 μm) were made to contact for sensor testing body that mounted on TO-8 header by microwelding method [62].

2.6 Carbothermal reduction

In a particular growth mechanism, 0.3 g zinc powder and 0.6 g effective carbon were adequately mixed in an agate mortar. The mixture was transferred into an alumina boat and kept in a horizontal muffle furnace at 900°C with 25°C/min for 2 h under normal pressure. Finally, the yellowish product formed and massed in the boat [63].

Carbothermal reduction technique can be used to synthesize ZnO NWs from graphite and ZnO powder in horizontal muffle furnace. At the downstream, the Si wafer sputtered with a 30°A Au coating. A rotary pump was used to evacuate the quartz tube at approximately 10^{-2} Torr, and Ar gas was introduced at 100 sccm. The temperature was increased to 900°C, and O_2 gas was introduced with 2 sccm for 30 min. After the growth of single crystalline ZnO NWs, an SnO_2 shell layer was deposited, and the temperature of the furnace cooled from 900 to 700°C. Tetramethyltin ((CH_3)$_4$Sn, 99.999%, UP Chemical Co., Ltd.) was kept in the quartz tube at 0.5 sccm of Ar as carrier gas and introduced with 2 sccm oxygen for 10 min [64].

2.7 Surface acoustic wave

The ZnO nanorod sensor was designed on Y-cut LiNbO$_3$ substrate for ethanol sensing. The performance of SAW is excellent due to electromechanical coupling coefficient ($k2 = 4.5\%$) offered by LiNbO$_3$ and small attenuation at high temperature. The interdigital transducers (IDTs) have a gap of 12 mm delay line, and each contains 50 pairs of electrodes. The width and the spacing inside the adjacent IDT electrodes are adjusted 15 μm. The IDT electrodes have length of 3 mm. The propagation of SAW elongated in x-direction of the crystal as IDTs is oriented on the surface of wafer.

Deposit a photoresistive layer by spin coated process and decorate it with window covering delay line for the construction of sensor. ZnO layer (100 nm) was sputtered with ZnO ceramic target by DC sputtering (conditions for sputtering, pressure = 2.7 Pa, in the presence of 80% argon and 20% oxygen) and the current required was 0.25 A DC. Acetone removed the photoresist layer leaving behind seed layer of ZnO. The devices were suspended with ZnO seed layer inverted in the solution of zinc nitrate, hexamethylenetetramine, and polyethylenimine. The bottle was incubated for 4 h at 95°C. The substrates were taken off from the solution, washed, and dried at room temperature [65].

3. Characterization

The characterization was done by using various spectroscopic techniques such as X-ray diffraction, scanning electron microscopy, and transmission electron microscopy for structural and morphological analysis.

3.1 X-ray diffraction

X-ray diffraction was done by a diffractometer of Rigaku D/max-2500 with Cu Kα radiation (λ = 0.15418 nm) and 2θ range from 20 to 80°, which confirm the hexagonal wurtzite structure of ZnO (JCPDS card no. 36-1451), the peaks are in agreement in Bragg reflections and no impurity peaks were observed [29].

3.2 Scanning electron microscopy

Surface morphology was done by Shimadzu SS-550 with a voltage of 15 kV. The ZnO rod-like nanostructure affirms from SEM images. High magnification revealed that ZnO nanorods have a length from 1.7 to 2.1 μm and diameter in the range of 90–200 nm.

3.3 Transmission electron microscopy

Transmission electron microscopy (Philips FEI Tecnai 20ST) at an accelerating voltage of 200 kV investigates the detailed structure of ZnO NRs [29].

The orientation of ZnO NRs was examined by X-ray diffractometer (Rigaku D/MAX B) utilizing Cu Kα radiation for post- and preannealing. The operating voltage and current were 40 kV and 40 mA, respectively. The measurement was conducted from 20 to 60° in the 2θ range with scanning rate 5°/min. Field emission scanning ELECTRON microscope (FESEM, JEOL JSM-7000F) was utilized to observe the morphology of grown ZnO nanorods. For sensitivity measurement, an ambient environment was controlled inside a chamber by flowing synthetic air.

The resistance was recorded by a Keithley 2400 SourceMeter (Keithley Instruments, Inc.) [42].

The top view of the ZnO NRs and cross-section morphologies were investigated by high resolution scanning electron microscopy (HR-SEM, S4200, HITACHI) and field emission (FE-SEM, XL-40FEG, PHILIPS). The crystal pattern of the NRs was revealed by X-ray powder diffraction (Rigaku MultiFlex) with a scanning step of 0.01° and scan speed of 4°/min. Fluorescence Spectrometer (MFS230) were used to determine the photoluminescent spectra of ZnO NRs at 325 nm excitation. The gas detection properties were investigated by measuring the resistance variation of the sensor in ambient air condition and ethanol mixed environment at 300°C [41].

A transmission electron microscopy (TEM: JEM-200CX, 160 kV, and HR-TEM: JEOL-2010F, 200 kV) was used to visualize the morphology of the grown Ag-ZnO NRs. 0.1 g of Ag-ZnO nanorod was ultrasonically suspended in ethanol 10 mL solution for TEM investigations. Then one drop of this solution is put on a copper grid with thin coating of carbon that evaporated at room temperature in air. An EDX analyzer (EDX: INCA OXFORD) was connected to the JEOL-2010F HR-TEM for in situ investigation of the configuration of the fabricated Ag-ZnO NRs. The elemental composition of Ag-ZnO NRs was further investigated by X-ray photo-electron spectrometer (XPS, PHI 5000C ESCA System, Perkin Elmer) with Mg Kα (λ = 1253.6 eV). The data investigation was done by RBD Auger Scan 3.21 software. Differential scanning calorimetry (DSC) analysis was carried out on a STA409PC thermal analyzer (Netzsch, Germany) with 10°C/min heating rate in air. The phase analysis of NRs was identified with powder X-ray diffraction analysis using a D/max 2550 V diffractometer with Cu Kα radiation (λ = 1.54056 Å) (Rigaku, Tokyo, Japan). One typical sensor containing Ag-ZnO NRs was further visualized by scanning electron microscopy (SEM: JSM-6700F, 10 kV) after working for 100 days [54].

The surface morphology visualization of the final product was investigated with a field-emission scanning electron microscopy (FESEM, JEOL JSM-6500F). The electrodeposited NRs have cross-sectional SEM image with 100–300 nm diameter and 1–2 μm in length. TEM low magnification image confirmed that ZnO NRs are well aligned in nature. Selected area electron diffraction (SAED) indicates that NRs are single crystalline ZnO with wurtzite structure. Energy dispersive analysis confirms the presence of Zn, O, Co, and Cu elements [44].

The crystal pattern of the ZnO NRs was revealed with X-ray diffraction (XRD, D8 Advance Bruker) with incident monochromatized radiation Cu Kα (λ = 1.5418 Å). XRD pattern was measured with a scanning step of 0.02°/s from 20° to 80° (2θ). Scanning electron microscopy (SEM, JSM-6301F) recorded the sizes of the samples and surface morphologies. SEM was operated at 20 KeV and transmission electron microscopy (TEM) investigation was done by H-800 transmission electron microscope that operated at 200 kV. The photoluminescence (PL) analysis was recorded at 325 nm (20 mW) by excitation with a laser emitter He-Cd at room temperature. The gas detection was determined by a China sensitivity instrument HW-30A. The gas response was evaluated by Ra/Rg, where Ra is the resistance in ambient air and Rg is the resistance in tested gas atmosphere [35].

Scanning electron microscopy (SEM, Holland Philips XL30) evaluates the surface morphology and crystalline size of Sm_2O_3-loaded ZnO samples. The EDX analysis evaluates the elemental composition of the synthesized samples. The crystalline pattern is recorded by the X-ray powder diffraction (XRD, Holland Philips) with Xpert diffractometer (CoKα = 1.7889 Å). The CHEMBET 3000 instrument was employed to record the specific surface areas (SSA) of the fabricated samples defaced at 330°C for 1 h utilizing Brunauer-Emmett-Teller (BET) technique. Diffuse reflectance UV-vis analysis for band gap evaluation was evaluated by an Avantes Avaspec-2048-TEC (using $BaSO_4$ as a reference) [56].

The morphology of ZnO NR surface was evaluated by scanning electron microscopy (SEM, FEI Nova Nano). X-ray diffraction (XRD) recorded the crystalline pattern and chemical composition of the seed layer as well as NRs deposited on the substrate. XRD was done by Bruker D8 Discover microdiffractometer equipped with a GADDS (general area detector diffraction system). The XRD was filtered with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes) that operated with a potential of 40 kV and a current of 40 mA. Data were recorded using Cu Kα radiation (λ = 1.54178 Å) at room temperature. The electrical characterization like conductivity of the sensor was measured with a multimeter (Keithley 2001) with various concentrations of ethanol in synthetic air. The information in real time was collected by data acquisition card attached to the computer with LabVIEW software. The gas mixture was supplied at the rate of 200 sccm and sensing done at a temperature range of 25–330°C [57].

The crystalline size and morphology of ZnO NWs were evaluated with field-emission scanning electron microscopy (FESEM, JEOL 6340F, operated at 5 kV). NW length and diameter were recorded with high-resolution SEM images. The phase analysis was explored with X-ray diffraction (XRD, Philips PW1730 diffractometer) with Cu Kα radiation [60].

Field-emission scanning electron microscopy (FESEM, JEOL model JSM-6700 F) was employed to evaluate the cross-sectional images and morphology of ZnO NRs. The NRs are distributed over the selected area uniformly and have hexagonal wurtzite structure with average length of 1.5 μm and diameter is about 55 nm. The crystalline pattern was recorded by X-ray diffraction using Cu Kα radiation. The electrical impedance spectroscopy (EIS) was done by Hioki LCR meter (model: 3532-50). EIS has AC signal amplitude of 50 mV with the frequency range from 42 Hz to 1 MHz. A two-electrode method was applied to determine the response of the ZnO NR sensor (working electrode) and counterelectrode as ITO was employed with a thin coating of Au [49].

The characterization such as X-ray powder diffraction (XRD, D/MAX2500, and Cu Kα radiation), scanning electron microscopy (SEM, JEOL JSM6700F), and transmission electron microscopy (TEM, JEOL 2010) determines the crystal pattern and surface analysis. The growth technique of the sensors based on the products has been described elsewhere [11, 12]. Briefly, the products were dispersed in ethanol, and a drop was spun on a ceramic tube between Pt electrodes to form a thin film (about tens of nanometers). A resistance heater in the ceramic tube was used to control the temperature. The sensitivity is defined as $S = R_a/R_g$, where R_a is the sensor resistance in air and R_g is the resistance in the target-air mixed gas [34].

Crystal pattern of the annealed ZnO NRs was characterized by X-ray diffractometer (XRD, DX-2700) using Cu Kα radiation (λ = 0.15418 nm) with 2θ range from 20 to 80°. The morphology, dimension, and surface details of the NRs were explored by scanning electron microscopy (FEI Quanta 200) that operated at 20 kV. The photoluminescence spectrum (PL, PE LS55 spectrophotometer) was recorded with 325 nm excitation from Xe lamp at room temperature. The sensing was done using a sensitivity instrument WS-30A (Wei Sheng Electronics Co. Ltd., China) with gas detection chamber of 30 L [58].

The effective limit of the sensor was found to be typically high (190–1530 ppm ethanol in air), for both kind of modified and unmodified NRs, with a saturation tendency beyond 1530 ppm ethanol (in air) [36].

X-ray diffraction (XRD, D8 Advance Bruker) analysis was conducted to calculate the crystal pattern with Cu Kα1 radiation (λ = 0.15406 nm) that operated at 40 kV. Field-emission scanning electron microscopy (FESEM, JEOL JSM-6700F) was performed to explore the surface morphology of the samples operating at a voltage of 5 kV. Transmission electron microscopy (TEM) pattern and selected area electron

diffraction (SAED) analysis were obtained by JEOL JEM-2010 microscope that was operating at an accelerating voltage of 200 kV. Photoluminescence (PL) spectrum was determined by Hitachi F-7000 FL Spectrophotometer with 325 nm excitation range at room temperature from Xe lamp. X-ray photoelectron spectrometry (XPS) was done by using Al Kα (hν = 1486.6 eV) with X-ray beams as the excitation source. Binding energies were calibrated relative to the C1s peak at 284.6 eV. The specific surface areas were measured via the Brunauer-Emmett-Teller (BET) method using an N2 adsorption at 77 K after treating the samples at 100°C and 10^{-4} Pa for 2 h using a Tristar-3000 apparatus [38].

4. Ethanol sensor performance characteristics

The different electrophysical properties exhibited by semiconductor metal oxides lie in the range from insulators to various band gap materials [20]. The conductivity of semiconducting materials like ZnO normally deviates from stoichiometry [27]. In the measurement of conductivity, vacancies of interstitial ions play an essential part. Sensors of semiconductor metal oxide work as a result of adsorption of gas on the sensing surface that cause in the variation of electrical resistance of ZnO. Due to charge concentration, semiconducting materials are categorized in n-type (like ZnO, TiO$_2$, WOx, MoO$_3$, TiO$_2$, CdO, and SnO$_2$) and p-type (such as NiO, TeO$_2$, and CuO) materials. The species of target gas can also be categorized into two types, oxidizing and reducing gases: oxidizing gas (electron acceptors) like NO$_2$ and O$_2$ and reducing gas (electron donors) such as CO, H$_2$, HCHO, H$_2$S, and C$_2$H$_5$OH. On the exposure of reducing gas on an n-type material surface, it chemisorbed and excess electrons are transferred to the surface of material. As a consequence, the material's resistivity reduced. The adverse effect is investigated in p-type materials. Such type of electrical adaptation was employed for gas sensing.

The important parameters of a sensor are sensitivity, recovery time, operating temperature, response time, and sensing smallest range as described in literature. Everywhere in the literature, sensitivity (S) of a sensor was illustrated in various ways consisting of S = Ra/Rg, S = Rg/Ra, S = ΔR/Rg and S = ΔR/Ra, where Ra is the sensor resistance in ambient air, Rg is the sensor resistance in the target gas, and ΔR = |Ra − Rg| [28, 66]. The investigation shows that sensitivity values are described as introduces by the author. The formula for measurement of sensitivity is also specifying. Response time can be stated as the time needed for a sensor to attain the original baseline 90% of the final response of the signal-like resistance on flow of required gas. The sensor recovery time can be stated as the time required returning 90% of the final signal on removal of target gas.

5. Design of gas sensor with 1D nanostructures

In the designing of nanogas sensors, 1D nanoarchitectures are used that contain metal oxide semiconductors in the structure of nanowires, nanotubes, nanorods, nanobelts, nanowhiskers, nanofibers, nanoneedles, nanoribbons, nanopushpins, fiber-mats, lamellar, urchin, and in the form of hierarchical dendrites. In all these structures, nanowires, nanotubes, nanofibers, and nanorods are rod-form nanoarchitectures with a diameter ranging from 1 nm to 200 nm. Nanowires and nanorods have aspect ratios from 2 to 20 and more than 20 [67]. Anyhow, the aspect ratio of nanofibers is greater than that of nanowires. Primarily, nanotubes are hollow nanorods with a determined thickness of walls. The interpretation of nanoarchitectures like nanowhiskers [25], fiber-mats [22], nanoribbons [24],

nanobelts [16], urchin [26], nanoneedles [23], lamellar [28], nanopushpins [27], and hierarchical dendrites [17] can be established in the appropriate literatures. It is essential to indicate that the difference among various nanoarchitectures is not forever understandable and is mostly conditions used alternately from one to another reference.

To design sensor, nanoarchitectures are arranged in various forms. Normally, nanostructures are arranged in electrode attachment technique. Generally, adjustment of nanostructures is divided into three forms such as: (a) single arrangement of nanostructures, (b) aligned, and (c) random adjustment. It has been investigated that in the detection of different gases like hydrogen single adjustment of nanofiber was used by researchers [68–70]. Due to various aspect ratios, the nanostructures may be in the form of nanowires or nanorods [5].

An in-situ lift-out method has been investigated by Lupan et al. to detect hydrogen gas for preparing single ZnO nanorod sensor. An electropolished tungsten wire is joined to a single ZnO nanorod, which is connected to external electrodes. In the way Lupan et al. [71, 72] and Hwang I-S [64] has also designed single tripod and tetrapod sensors with the help of in-situ lift-out process by FIB. For nano-/ microsensors depending upon nanostructures from semiconductor metal oxides, their process gained a 90% progress rate.

Liao et al. fabricate a gas sensor for ethanol detection in which zinc oxide nanorod arrays were used inside an indium thin film and silicon substrate [71, 72]. Ohmic contact is provided by an indium film, and for electrode, copper sheet was used. Arbitrary separated nanostructured sensors have alterations such as (a) distribution of nanostructures randomly in the film shape, (b) arbitrary separation of nanostructures' drop on the circumference of a tube, and (c) random distribution of nanostructures pressed in tablet shape. Flat interdigitated substrate was used by Wan et al. where arbitrary distribution of zinc oxide nanowires were dissolved by ultrasonication in ethanol and then spin coated on silicon interdigitated substrate. Occasionally, fabrication and attachment of nanowires with substrate are integrated with the device construction [73–75].

The tube-shaped sensors are modification of film-shaped arbitrary distributed nanostructured sensors; hence, the smooth surface is the form to a tube. Such kind of sensor has a ceramic tube-type substrate. Normally, Al_2O_3 is used as tube material and the surface is coated with one-dimensional gas sensing materials. Different types of one-dimensional gas sensing materials having various morphologies may be used on the surface of the tube. Hao et al. [26] designed a tube-shape sensor for H_2S sensing.

To design tablet-shaped sensors, randomly separated nanostructures can be used. Ethanol sensing was done by such detectors as reported by Zhou et al. [47]. At 6 MPa pressure, ZnO nanorods were grown in pellets form with thickness of 5.3 cm^2 areas and dimension of 3 mm. Electrodes were made from silver paste at the back and front surface of the ZnO pellets.

5.1 Gas detection from nanostructural materials

Nowadays, due to fine crystallinity, high aspect ratio and charge detection capability of one-dimensional nanostructure materials have become intensified for gas detection applications.

Various routes have been adopted for the synthesis of 1D nanostructures for gas detectors. The cost, yield, quality of the materials, and complexity differ for various processes. The metal oxides TiO_2, ZnO, WOx, SnO_2, CdO, In_2O_3, CuO, Fe_2O_3, $AgVO_3$, TeO_2, and MoO_3 have been studied for various required gases with

different sensitivity. Here, we discuss ZnO 1D nanostructures in terms of their fabrication, characterization, and sensitivity for sensing ethanol.

6. Performance of ethanol sensors

The ZnO NRs were then used to construct a gas sensor for ethanol sensing at various working temperature from 200 to 340°C. The as-prepared ZnO nanorod gas sensor exhibited a high, reversible, and fast response to ethanol, indicating its potential application as a gas sensor to detect ethanol. It is obvious that with the increase of ethanol concentration the response increases [29].

Flexible ZnO nanorod sensors were examined to monitor ethanol gas by varying the working temperature from 300°C to by changing the ethanol concentration in a range from 100 to 10 ppm in synthetic air. The sensitivity of a gas sensor is not influenced by the thickness of the seed layer, which presents that density of the charge carrier of ZnO NR is responsible for gas detection properties. The dimension of NRs plays an essential part in evaluating the sensitivities. A flexible ZnO nanorod sensor can detect 100 ppm of ethanol gas with a sensitivity of 3.11 at 300°C [42].

Due to large aspect ratio, the response of ZnO NRs to ethanol gas is better than that of the ZnO seed layer sensor. There are more free electrons taking part in the sensing processes with adsorbed oxygen species for the NRs grown with Zn salt/ KOH solution. Therefore, a better sensitivity of the NRs grown with Zn salt/KOH solution to ethanol gas is mainly a result of the more free carriers originating from oxygen vacancies in sensor materials. The Schottky or ohmic contact shows that Au has more work function than ZnO. Hence, the sensor exhibiting the Schottky contact has a better response to ethanol gas than possessing an ohmic behavior. In conclusion, the free electrons are an important parameter for increasing the sensor response beside large aspect ratio [41].

The response of ZnO NRs decorated with photochemical Ag NP sensor to 50 ppm ethanol is almost three times as high as that of those made from pure-ZnO NRs. The electronic sensitization of noble metal doping like Ag is comfortable to grow stable oxide (Ag_2O) at operating temperature (280°C) in air. The adsorbed O_2 on the surface of Ag_2O extracts electron from ZnO and produces a depletion layer. After exposing to some target gases, Ag_2O reduced to Ag and eventually gives ZnO. Hence, due to increase in charge carrier, the sensitivity of the sensor enhanced. The responses of the sensors have no apparent degradation after being exposed to ethanol of 30 ppm for 100 days [54].

The doped ZnO sensors show increased sensitivity as compared to undoped conditions. It is shown that the sensitivity was highly affected by both Co doping and its concentration. The sensor response has been boosted by a factor of 1.6 and 1.8 for 1.85 at.% Co (Sg = 10.9) in comparison with 0.76 at.% (Sg = 6.7) and by undoped conditions (Sg = 6) in ZnO NRs, respectively, for 50 ppm C_2H_5OH [44].

The response of gas sensor based on n-type semiconductor ZnO nanorods exposed to various concentrations of the ethanol vapors at 400°C has been investigated. It showed a considerably high response even at low concentration of 5 ppm ethanol. Their response and recovery times were less than 10 and 30 s, respectively. In addition, the sensors were still sensitive to 5 ppm ethanol, even after exposure to 300 ppm ethanol. The reversible cycles of the response curve indicate a stable and repeatable operation of gas sensing. The much higher sensitivity may be due to the large effective surface areas. The results revealed that ZnO NRs show excellent response and stability. The higher response may be due to greater surface area [35].

The resistance of the sensor significantly enhanced in air at the small temperature of 200°C, due to samaria contents. A 10 times further increase in the resistance of ZS-10 consisting of 10 wt% Sm_2O_3 is investigated.

At the small temperature of 200°C, the sensor resistance in air significantly increases with samaria contents. A 10 times more increase in the resistance of ZS-10 consisting of 10 wt% Sm_2O_3 is investigated. At greater value of temperatures from 250 to 350°C, the ZS-5 and ZS-10 have the same resistances, yet greater than those of ZS-2 and Z. The main work of samaria is perhaps placed on the ZnO surface, averting direct interaction with ZnO nanoparticles that as a result enhanced the Schottky barrier. The analysis of ZnO by 10 wt% Sm_2O_3 is perhaps liable for the greater resistance explored for this sample. These investigations are explained with DRS UV-vis. The sensitivity of the Sm_2O_3-ZnO sensor was observed in the presence of 500 ppm of CO, toluene, and ethanol and 1.0 vol% of methane at a temperature of 200–400°C in air for Sm_2O_3. A significant increase in the ethanol response was investigated at different temperatures due to 5 wt% doping of Sm_2O_3-ZnO, although a smaller one toward toluene, methane, and CO. A 60 times greater response was observed to ethanol with 5 wt% Sm_2O_3-ZnO as compared to that of pure ZnO sensor [56].

A rapid and repeatable detection was observed toward ethanol vapors at normal temperature and 330°C. At an operating temperature between 280 and 310°C, the sensor has excellent response with a detection time to 500 ppm ethanol and in a time from 16 s to 120 s. High sensitivity, fast recovery, and response time have been explored at this temperature limit. The results investigate that the constructed sensor is a potential candidate for industrial applications and promising for commercialization [57].

The research explores the ZnO growth environment that explains the properties related to opto-geometry of the random ZnO nanorods over layer and the spectral response is dominating over the long time grating device. The response of ethanol toward ZnO-overlaid LPGs was confirmed under various fabrication conditions and also their spectral response correlating with available simulation models [59].

The sensor resistance enhanced with the flow of ethanol on the surface of the sensor. The sensor response time (which is defined as the 90% of the full response) is small and changes from 200 to 125 s as the concentrations enhanced from 809 to 4563 ppm, and it was investigated that the recovery time is approximately 10 min [60].

The result presents that high sensing characteristic has been established by ZnO-based sensor in the ethanol concentration (1–99.5%). The conduction process depends upon internal resistance of the nanorods for small value of ethanol concentration (a semicircle at high frequency). The charge transfer resistance interior the grain boundaries shows a straight line at small frequency region. I-V characteristics determine the sensitivity of ZnO sensor. ZnO NR arrays have potential to fabricate a chemical sensor with small power consumption and high sensitivity [49].

The recovery time response and response were established in the range of 15 and 5 s for 95% of total recovery and response, respectively. The porous structure of the sensing material is responsible to this phenomenon. The molecules diffused easily into and out of the sensing materials than did the dense structures [65].

The response enhanced from 7 to 9 with increase in temperature from 160 to 300°C. Hence, it enhanced drastically when temperature attains a value of more than 300°C. The value of the response varies from 9 to 24 as the temperature changes from 300 to 340°C and then attains the maximum value of 34 at a temperature of 370°C [58].

The SAW sensor for ethanol detection constructed from ZnO nanorods exhibits a frequency of 24 kHz at 270°C to 2300 ppm ethanol response, which is an improvement of 9 kHz of the sensor without nanorods [65].

It was investigated that a large surface energy and greater amount of O_2 vacancies' concentration exist in the NA and NHS surface that increased the ethanol detection characteristics at small temperature [53].

The conductivity of Ti-ZnO sensor was greater than that of the pure ZnO NRs by a factor of 80.7 that is 1.86%. The ethanol gas sensing response of the ZnO:Ti NR sensor has a linear relationship with temperature. The responses were found at 27.5, 66.7, 117.1, 183.5, 276.5, and 389.5% with 10, 50, 100, 250, 500, and 1000 ppm ethanol concentration, respectively. It was investigated that the responses of ZnO:Ti NR sensor are greater than those of the ZnO NRs at 1000 ppm ethanol concentration by about 5.1 [61].

It was demonstrated that they exhibited good performance for detecting ethanol vapor even at 380 and 250°C [48].

It is confirmed from the experimental results that there is no noticeable degradation of the sensor response after the flow of 50 ppm ethanol for consecutive 60 days at the operating temperature [63].

The response to 10 ppm NO_2 became negligibly small (2.3) compared to that at 200 and 300°C (66.3 and 12.4). This shows that with enhancing temperature at 400°C the capability of C_2H_5OH sensing increases. The selective detection was investigated with ZnO NWs by 200 ppm C_2H_5OH as compared to that with ZnO-SnO$_2$ core shell NWs only at a limit of 1/7 [64].

The research results show that from a temperature of 300°C the gas response increases abruptly till it attains the maximum value of 400°C. Then, the response decreases rapidly to a temperature limit of 400–430°C. The smaller value of working temperatures (300–400°C), 400°C, was investigated as the OOT for the ZnO NR sensor with 200 ppm ethanol response was observed to have a value of 193.7 [38].

The addition of detection layers in ZnO shows greater value of sensitivity with greater stability/reproducibility to ethanol, and comparatively small response and recovery time relative to the pure layer of MoO_3. Ethanol sensing increased with the impurity (Gethanol/Gair). The 25% ZnO in the presence of MoO_3 layer as impurity for 500 ppm ethanol attains a level of 171 under nonhumid air. Its response under humid air is 117 (75% r.H. at 21°C). This response is 6 times greater than that for the pure MoO_3 layer [62].

The sample has approximate response and recovery time of 3 and 4 min, respectively. As regard the detection characteristics of other ZnO nanoarchitectures working at greater temperatures, the ZnO NR sensors have high response and recovery time when operated at room temperature [47].

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