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Formulation and Characterization of Cr_2O_3 Doped ZnO Thick Films as H_2S Gas Sensor

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Abstract: Cr_2O_3 doped ZnO thick films have been prepared by screen printing technique and firing process. These films were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), and EDX. H_2S gas sensing properties of these films were investigated at different operating temperatures and different H_2S concentrations. The 7 wt. % Cr_2O_3 doped ZnO thick films exhibits excellent H_2S gas sensing properties with maximum sensitivity of 99.12 % at 300 ^oC in air atmosphere with fast response and recovery time. *Copyright © 2009 IFSA.*

Keywords: ZnO, Cr_2O_3, Thick films, Screen printing, H_2S

1. Introduction

Metal oxide semiconductor gas sensors have been used extensively to detect toxic, pollutant hazardous and combustion gases [1, 2]. The semiconducting metal oxides such as SnO_2, ZnO, Fe_2O_3, WO_3 etc. offer the potential for developing portable and inexpensive gas sensing devices, which have advantages of simplicity, high sensitivity and fast response. The working principle of these semiconductor gas sensors is based on change in conductivity when exposed to the target gases [3]. Among the various materials, ZnO is most promising semiconductor metal oxide to detect toxic and hazardous gases [4-8]. It is sensitive to many sorts of gases and has satisfactory stability. However these sensors are not selective for a particular gas and various attempts are being made to improve their selectivity. One approach is to use dopants and additives [9-13] which can modulate the gas sensing characteristics to some extent. The methods to improve the selectivity of sensor include the use of masks and filters or temperature programming where temperature is carefully controlled so that sensor detects only a particular gas with high sensitivity.

Hydrogen sulphide (H_2S) is toxic in nature. It is important to monitor and control it in laboratories and industrial areas where it is used. Some well known materials for H_2S gas sensing are SnO_2-ZnO [14], SnO_2 [15], BST [16] films. It has been studied that Cr_2O_3 was used as a gas sensing element [17, 18]. The aim of present study is to prepare Cr_2O_3 doped ZnO thick films by standard screen printing technique on alumina substrate and to investigate their sensing properties for H_2S gas.

2. Experimental

The ZnO:Cr_2O_3 pastes used in screen printing were prepared by maintaining the inorganic to organic materials ratio of 70:30. The inorganic part consists of a functional material (ZnO), dopant (Cr_2O_3) and glass frit (70 wt.% PbO, 18 wt. % Al_2O_3, 9 wt. % SiO_2 and 3 wt.% B_2O_3). The organic part consists of 8% ethyl cellulose (EC) and 92 % butyl carbitol acetate (BCA). The AR grade ZnO with x wt. % Cr_2O_3 (x = 1, 3, 5, 7 and 10 %) and 5 wt. % of glass frit were mixed thoroughly in an acetone medium with mortar and pestle.

A solution of EC and BCA in the ratio 8:92 was made, which was added drop wise until proper thixotropic properties of the paste were achieved. ZnO thick films were prepared on alumina substrate by using standard screen-printing technique. The screen of nylon (40 s, mesh no.355) was used for screen-printing. The required mask (2 x 1.25 cm) was developed on the screen by using standard photolithography process. The pattern was allowed to settle for 15 to 20 minutes in air. The films were dried under IR radiation for 45 minutes to remove the organic vehicle and then fired at temperature 700 ^oC for 2 hrs (includes time required to achieve the peak firing temperature and then maintain constant firing temperature for 30 minutes at peak value and decrease to attain the room temperature) in muffle furnace.

During the firing process glass frit melts and the functional material and dopant are sintered. The function of glass frit is to bind the grains of functional and dopant materials together and also to adhere the film firmly to the substrate surface. The structural properties of ZnO films were investigated using X-ray diffraction analysis from 20-80^0 [Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having CuKα, λ=0.1542 *nm* radiation] with 0.1 ^{o}/step (2θ) at the rate of 2 sec/step.

The scanning electron microscopy (SEM- JOEL JED-2300) was employed to characterize the surface morphology. The composition of ZnO thick film samples were analyzed by Energy Dispersive spectrometer (JOEL-JED 6360 LA). The thickness of the ZnO thick films was measured by using Taylor-Hobson (Taly-step UK) system. The thickness of the films was observed uniform in the range of 20 μm to 22 μm. The D.C. Resistance of the films was measured by using half bridge method in atmosphere at different temperatures. The gas sensing studies were carried out on a static gas sensing system under normal laboratory conditions. The H_2S gas response of thick films was studied in test assembly. The electrical resistances of ZnO thick film in air (R_a) and in the presence of H_2S gas (R_g) were measured to evaluate the gas response (S) given by the relation,

$$S = \frac{R_a - R_g}{R_a}, \tag{1}$$

where R_a is the resistances of the ZnO thick film sample in air and R_g is the resistances of the ZnO thick film sample in H_2S gas atmosphere.

3. Result and Discussion

3.1. Elemental Analysis

The quantitative elemental compositions of the pure and doped ZnO films were analyzed using an energy dispersive spectrometer. The mass % of Zn and O in each sample were not as per stoichiometric proportion. The entire samples were observed to be oxygen deficient. The film doped with 7 % Cr_2O_3 was observed to be most oxygen deficient. The deficiency or excess of the constituent material results in distorted band structure with corresponding increase in conductivity. Zinc oxide loses oxygen on heating so that the zinc is in excess. The oxygen of course evolves as electrically neutral substance so that it is associated with each excess zinc ion in the crystal; there will be two electrons that remain trapped in the solid material, thus leading to non-stoichiometricity in the solid. This leads to the formation of the semiconducting nature of the material [19].

3.2. Structural Analysis

The crystalline structure of the films was analyzed with X-ray diffractogram in the 20-80^0 (2θ) range using Cuk$_\alpha$ radiation. Fig. 1 depicts the XRD pattern of undoped and Cr_2O_3 doped ZnO thick films of different concentrations. The peaks in XRD patterns observed for ZnO, Cr_2O_3, $ZnCr_2O_4$ and are polycrystalline in nature.

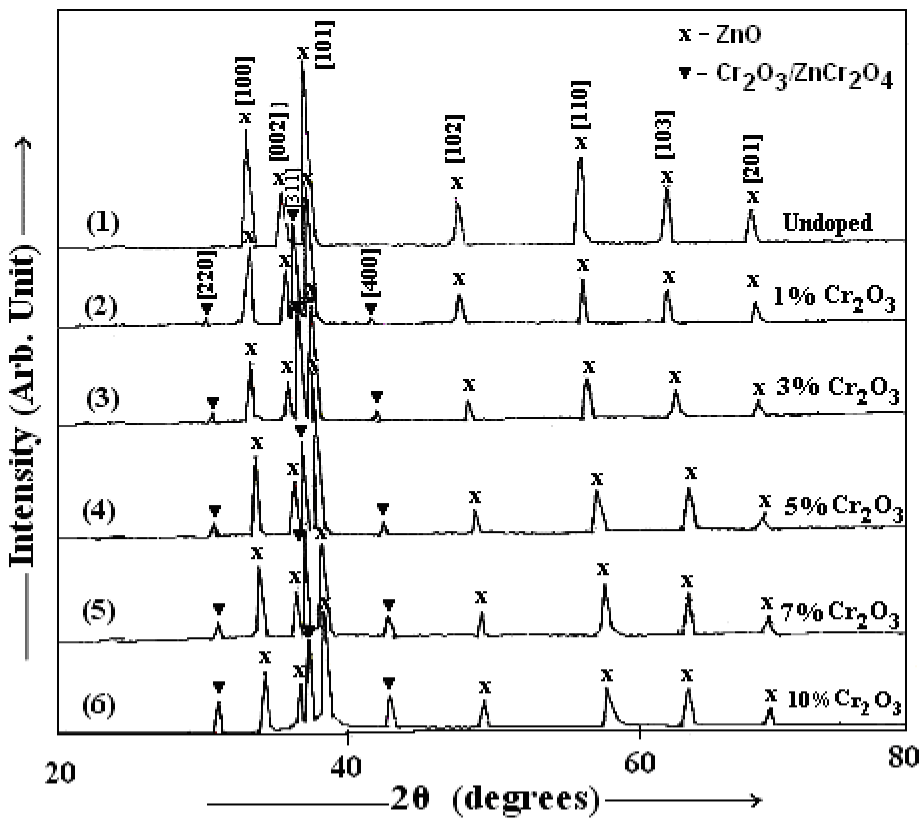
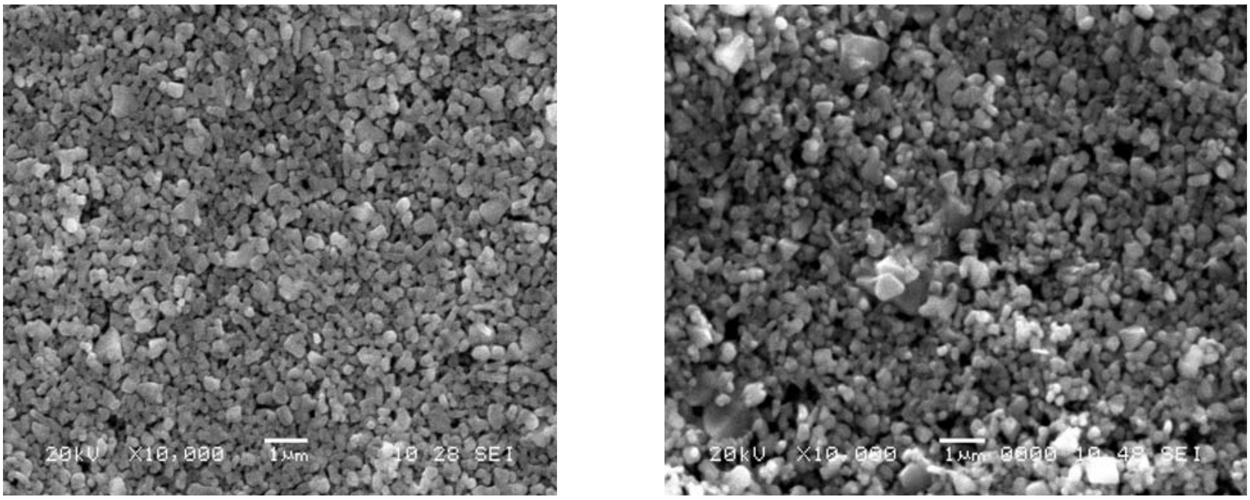


Fig. 1. XRD pattern of undoped ZnO and Cr2O3 doped ZnO films.

3.3. Surface Morphology Analysis

Fig. 2 depicts the SEM images of pure and Cr_2O_3 doped ZnO thick films. Fig. 2 (a) shows the microstructure of pure ZnO thick film. It consists of randomly distributed grains with smaller size and shape distribution. Fig. 2 (b) depicts the microstructure of 7 % Cr_2O_3 doped ZnO thick film which was most sensitive. It consists of giant particles of Cr-species distributed on the ZnO grains. The film seems to be highly porous for oxygen adsorption.



(a) (b)

Fig. 2- SEM images of (a) pure ZnO (b) 7 % Cr_2O_3 doped ZnO films fired at 700 ^0C

3.4. Gas Response

3.4.1. Response of Pure and Doped ZnO Films

Fig. 3 shows the variation of sensitivity of pure ZnO and 7 wt. % Cr_2O_3 doped ZnO thick films fired at 700 ^oC exposed to 1000 ppm of H_2S gas with operating temperature. The sensitivity increases with operating temperature from 150 to 300 ^0C and then decreases with a further increase in temperature. The sensitivity of pure ZnO thick film to H_2S gas was found to be 10.46 % at 350 ^0C where as the sensitivity of 7 wt. % Cr_2O_3 doped ZnO thick film to H_2S gas was found to be 99.12 %. Pure ZnO is notably less sensitive than modified ZnO.

3.4.2. Effect of Doping Concentration on Gas Response with Operating Temperature

Fig. 4 shows variation of the sensitivity with operating temperature for different wt.% of Cr_2O_3 doped in ZnO and exposed to 1000 ppm of H_2S gas in air. The sensitivity of 7 wt. % Cr_2O_3 doped ZnO thick film was observed as highest at 300 ^0C. The higher response may be attributed to the optimum porosity and largest effective surface area available to react the gas. The response could be attributed to the adsorption – desorption type of sensing mechanism. The amount of oxygen adsorbed on the surface would depend on the number of Cr_2O_3 misfits to adsorb the oxygen which in turn would oxidize the exposed gas.

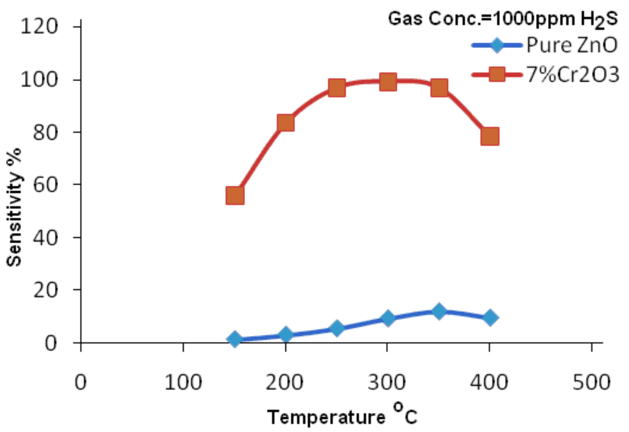


Fig. 3. Variation of sensitivity with operating temperature for pure ZnO and 7 wt. % Cr_2O_3 doped ZnO thick films fired at 700 °C exposed to 1000 ppm of H_2S gas.

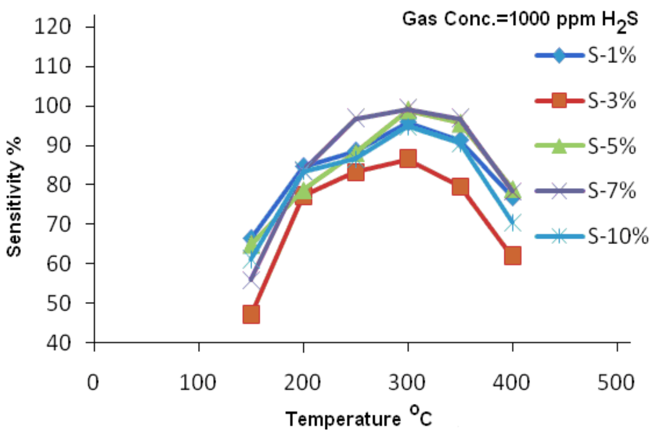


Fig. 4. Variation of the sensitivity with operating temperature for different wt. % of Cr_2O_3 doped in ZnO thick films exposed to 1000 ppm of H_2S gas.

3.4.3. Selectivity of Cr_2O_3 –doped ZnO Films for Different Gases

Fig. 5 shows the selectivity of 7wt. % of Cr_2O_3 doped ZnO thick film for different gases. Sample showed highest selectivity for H_2S gas at 300 ^{0}C against all other tested gases viz: NH_3, LPG. Ethanol vapours, CO_2, NO_2.

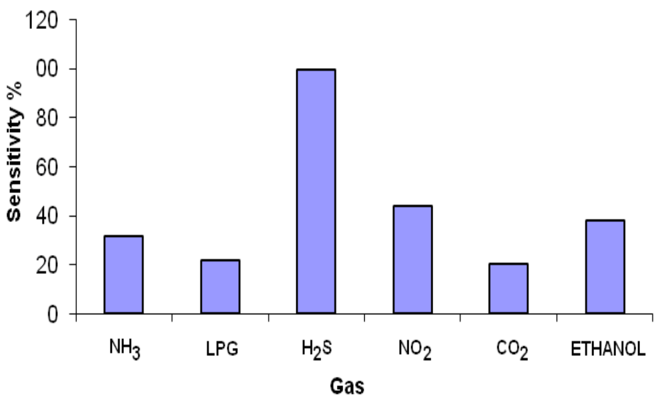


Fig. 5. Selectivity of 7 % Cr_2O_3 doped ZnO thick film for different gases.

3.4.4. Effect of H_2S Gas Concentration on Gas Response

Fig. 6 shows the variation of sensitivity of the 7 % Cr_2O_3 doped ZnO film with H_2S gas concentration at 300 ^oC temperature. This film was exposed to different gas concentrations of H_2S. The sensitivity values were observed to increase linearly with increasing the gas concentration up to 300 ppm and the rate of increase become smaller during 300 and 1000 ppm. The response is maximum for 1000 ppm. The monolayer of the gas molecules formed on the surface could cover the whole surface of the film. The excess gas molecules would remain idle and would not reach the surface active sites of the film. So, the response at higher concentrations of the gas is not expected to increase in large extent.

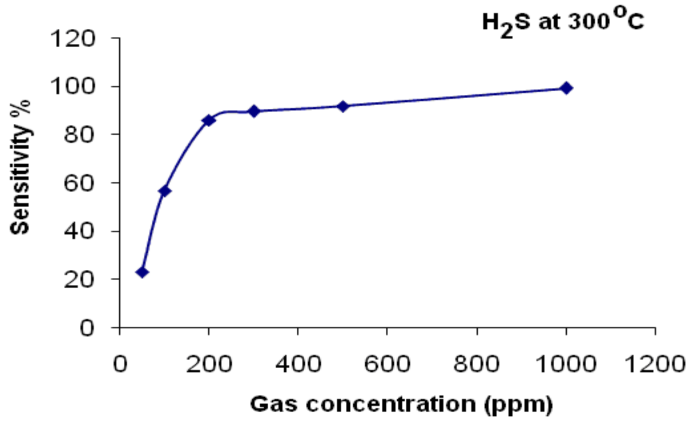


Fig. 6. Variation of gas Sensitivity with gas concentration.

3.4.5. Response and Recovery Time

The response and recovery times of 7 wt. % Cr_2O_3 doped ZnO thick films are represented in Fig. 7. The response was quick (~ 11 sec) to 1000 ppm of H_2S while the recovery was fast (~ 13 sec). The quick response may be due to faster oxidation of gas. Its high volatility explains its quick response and fast recovery to its initial chemical status.

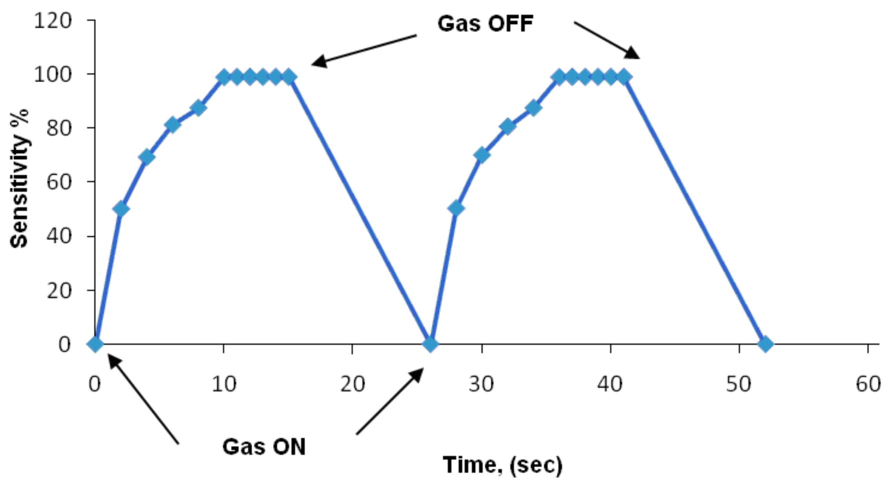


Fig. 7. Response and recovery of 7 % Cr_2O_3 doped ZnO film.

3.5. Sensor Mechanism

In the presence of test gases, the electrical conductivity of porous semiconductor thick film sensor changes due to two main reactions occurring on the surface.[20, 21]. These reactions are the adsorption of atmospheric oxygen on the surface and the direct reaction of lattice oxygen or interstitial oxygen with test gases. In the first reaction, atmospheric oxygen molecules are physisorbed on the surface sites, which while moving from site to site, get ionized by taking an electron from the conduction band and are thus ionosorbed on the surface as O^{-}_{ads} [20, 22]. This causes decrease in conductance of sensor material. The resulting equation is,

$$O_2 + 2e^- \rightarrow 2O^-_{ads} \tag{2}$$

In ZnO films, electrons are also extracted from the interstitial zinc atoms Zn_i^{2+}, which act as an electron donor[20, 23]. The interstitial zinc atoms in such cases are ionized via the following reversible reaction,

$$Zn_i^{2+} \leftrightarrow Zn_i^{+} + e^- \tag{3}$$

In the second step the reducing gas (R) present in air ambient reacts with the chemisorbed oxygen, thereby releasing an electron back to the conduction band and increasing the conductance of the semiconductor,

$$R + O^-_{ads} \rightarrow RO + e^- \tag{4}$$

At higher temperature RO desorbs.

The catalyst used dispersed on the surface of the grains of the sensor material activates the reducing gas and allows it to spill over onto the sensor material. Thus the resulting change in conductance in Eq.(4) is enhanced.

Cr_2O_3 doped ZnO thick films consist of number of grains of Cr_2O_3 (misfits) and ZnO connected to each other through grain boundaries. This leads to the formation of barrier height among the grains and increases the resistance in the absence of the target gas [24].

The H_2S gas is reducing in nature. It reduces Cr_2O_3 into Cr_2S_3 or CrS, which are metallic in nature and more conducting than Cr_2O_3. This can be represented as:

$$Cr_2O_3 + 3\,H_2S \rightarrow Cr_2S_3 + 3H_2O \tag{5}$$

or

$$4Cr_2O_3 + H_2S \rightarrow 8CrO + 3SO_2 + H_2O \tag{6}$$

$$CrO + H_2S \rightarrow CrS + H_2O \tag{7}$$

Due to the reduction of chromium oxide into sulphides, the film resistance would decrease suddenly and largely. This can be attributed to the high response of Cr_2O_3-doped ZnO film to H_2S. Upon the subsequent exposure of sensor to air ambient at elevated temperatures; sulphides got oxidized and could be recovered back to oxides as:

$$2Cr_2S_3 + 9O_2 \rightarrow 2Cr_2O_3 + 6SO_2 \tag{8}$$

$$2CrS + 3O_2 \rightarrow 2CrO + 2SO_2 \tag{9}$$

The separate chemical identities (Cr_2O_3) on the surface can create artificial surface states in the midgap region, leading to unusual physical and chemical properties. For example, the adsorption energy can be higher for the misfit regions, and the discontinuity in the adsorption potential can give rise to unusual selectivity effects for Cr_2O_3 doped ZnO based semiconducting oxide sensors. There would be optimum number of Cr_2O_3 misfits (in case of 7 wt. % Cr_2O_3 doped film) distributed uniformly on the surface of the film. Cr_2O_3 misfits could act as catalyst for oxygenation leading to an increase in resistance by electron transfer from surface state to oxygen species. Due to the Cr_2O_3 misfits, the number of oxygen ions adsorbed on the surface would be largest. When H_2S gas comes in contact with Cr_2O_3 doped ZnO surface, it undergoes oxidation releasing electrons, decreasing resistance of the sensor and enhancing the response to H_2S [25].

4. Conclusion

From the results obtained, following conclusions can be made for the sensing performance of Cr_2O_3 doped ZnO thick films:

(1) It has become possible to make thick film gas sensors using screen printing method.
(2) Pure ZnO thick films showed low response to H_2S gas.
(3) 7wt. % Cr_2O_3 doped ZnO thick films showed highest response to H_2S gas at 300 ^{0}C.
(4) The sensitivity increases in proportion to the test gas concentration.
(5) The sensor has good selectivity to H_2S gas against LPG, NH_3, Ethanol vapour, CO_2 and NO_2 at 300 ^{0}C.
(6) The sensor showed very rapid response and recovery to H_2S gas.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
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- Technologies and materials;
- Nanosensors;
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