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SHORT PAPERS

Chemically Modified NiO Gas Sensor for Environmental Monitoring

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Abstract: In this work, we report semiconducting nanocrystalline NiO and Pd-doped NiO sensor with high sensitivity and excellent selectivity for H2S gas. These nanomaterials were synthesized by the solution based technique. Related structural and electrical properties of doped and pure NiO thick films were studied used to XRD, XPS, SEM, EDX, BET/BJH and impedance technique. The gas sensing characteristics of pure NiO and Pd-doped NiO were compared using a homemade gas sensing measurement system. The sensitivity, operating temperature, and response/recovery time were systematically investigated based on the change in electrical resistance of the materials in the presence of reduced gas (H2S, CO, LPG and ethanol) environment. Experimental results confirmed that gas sensitivity was enhanced by doping different concentration of Pd in NiO thick films. The 5 wt% Pd doped NiO thick film sensor showed a maximum response to 20 ppm H2S (93%) at an operating temperature of 60 °C.

1 INTRODUCTION

Hydrogen sulfide (H2S) is a colorless, poisonous, flammable gas with the characteristic foul odour of rotten eggs. H2S gas takes part in many industrial processes, which is a highly reducing gas and heavier than air, and it is produced as a by-product in more than 70 industries (Balamurugan and Lee, 2015). Human expose of high levels of H2S can cause death (Struve *at al.,* 2001). Health effect also have found in human longer exposed to low-level concentration of H2S will lead to chronic poisoning symptoms, such as hypoesthesia, losing weight, headache, fatigue and so on (Yu, Ning and Qian, 2010). In addition, human bodies produced small amount of H2S and act as a signalling molecules. Moreover, H2S produced endogenously in mammals, including human and has various physiological effect on the human body. For example, H2S is physiologically produced by cystathionine-γ-lyase (CSE) and cystathionine-β-synthase (CBS). These are dependent on pyridoxal-5'-phosphate enzymes, which are expressed in the liver, kidney, brain, thoracic aorta, ileum, pancreatic islets, uterus, and placenta, among other locations, are crucial in the synthesis of H2S. CBS is predominantly expressed in the brain and the nervous system. However, expression of CSE proteins has been mainly observed in vascular smooth muscle cells and in the heart (Zhang *at al.,* 2013) Therefore, monitoring and detection of low level H2S is a very important requirement in various fields, such as industrial area, human body and biological environment. The high cost of the sophisticated analytical instruments systems (e.g., spectroscopic gas sensor, optical gas sensor, mass chromatography and mass spectrograph) limits the control and monitoring of the H2S level. However, semiconductor metal oxide is one of the most alternative ways for H2S detection applications.

Semiconductor metal oxides such as ZnO, CuO, SnO2, and In2O3 are widely used as gas sensors based on the change in their electrical conductivity on exposure to the test gases. Beyond the most investigated metal oxides, NiO metal oxides have attracted considerable interest due to their unique structural and electrical properties. Many attempts were presented to significantly enhance the NiO sensing performance by design and implementation of novel structures, which are determinative for the absorption/desorption, charge-transport path, surface area, and electrical conductivity. However, they have some disadvantages, such as a high working temperature, poor selectivity and limited time stability. Therefore, by introducing the noble metal nanoparticales is one of the ways to enhance the sensitivity and selectivity of the base materials

(NiO). In this work, we describe the fabrication, characterization and application of semiconductor NiO nanopowder and different weight % Pd doped NiO nanopowder for H_2S gas sensing applications. NiO and doped metal oxide nanopowder were synthesized via the metal-citrate complex method. Related structural and electrical properties of doped and pure NiO nanopowder were studied using to various characterization technique. The H_2S sensing characteristics of pure NiO and Pd-doped NiO nanopowder based sensor were compared using a homemade gas sensing measurement system. The experimental results confirmed that the 5 wt% Pd doped NiO nanopowder based sensor showed a maximum response to 20 ppm H_2S (93%) at an operating temperature of 60 °C. The selectivity of the sensor elements for H_2S against different interfering gases such as CO, ethanol and LPG was studied.

2   EXPERIMENTAL

2.1   Synthesis of 5 Wt% Pd Doped NiO Nanopowder

All chemicals used in our experiments were reagent grade and used without further purification. In a typical our experiment, initial solutions were prepared by dissolving stoichiometric mole ratios of nickel nitrate, palladium nitrate and citric acid into 100 mL of deionized water. The mixture was stirred at room temperature for about 1 h until the mixture become homogeneous. Then, catalytic amount of CTAB, PVA and ethylene glycol were added, and the pH value of the mixture was adjusted to 7 using NH_3 solution with vigorous stirring for 1 h. The resulting mixture was heated on a hot plate with continuous stirring; the solution boiled and underwent dehydration, followed by decomposition, with the evolution of large amounts of gases. The produced powder was calcined by a gradual increase of temperature up to 600 °C and was kept in air at that temperature for 2 h to obtain 5 wt% Pd doped NiO nanopowder.
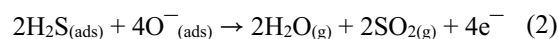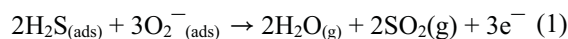
2.2   Fabrication of Sensor Element

The fabrication of the H_2S gas sensor was performed as follows. The prepared nanopowder was mixed with a suitable amount of adhesive (ethyl cellulose and terpinol) and hand-ground in an agate mortar to form a paste. The prepared paste was then laid uniformly on the surfaces of ceramic tubes, with a coating thickness of approximately 50 µm. The sensor response S defined as S= $(R_{gas}-R_{air})/R_{air}$ X 100% where, R_{air} is the resistance of the sensor in the air and R_{gas} is the resistance of the sensor in the presence of the test gas.

3   RESULT AND DISCUSSION

XRD patterns of the NiO and 5 wt% Pd doped NiO precursor samples calcined at 600°C for 2 h, are shown in Fig. 1 (a, b). As observed, all the diffraction peaks can be well assigned to the cubic structure with a space group of Fm3m, which are in agreement with the standard JCPDS data (Card No. 73-1523). In Fig. 1 (b) the peaks emerged at 2θ values of 34.62° and 55.43°, for the 5 wt% Pd doped sample, indicates the Pd metal atoms are efficiently dissolved in the NiO host lattice. The calculated lattice parameter, a = 4.180 °A was well matched with the standard lattice parameter values. Moreover, the sharpness of the patterns corresponding to the NiO and 5 wt% Pd doped NiO nanopowder indicated that high levels of crystallization occurred. The calculated average grain size well coincides with the broadening of XRD peaks. The average crystallite size of the 5 wt% Pd doped NiO nanopowder is lower than the grain size for the NiO nanopowder. Furthermore, BET surface area of the NiO nanopowder is 45.25 m^2/g and that of the 5 weight percent Pd doped NiO nanopowder is 56.35 m^2/g. The prepared nanopowders were subjected to gas sensor studies with test gas like H_2S by measuring sensor response as a function of various operating temperature as shown in Fig.2. The response increased linearly with increasing temperature. The response of the 5 wt% Pd doped NiO based sensor to 20 ppm of H_2S gas was higher (93%) than that of NiO, meaning that the 5 wt% Pd doped NiO material was highly reactive for H_2S gas. Furthermore, the sensor based on NiO and 5 wt% Pd doped NiO nanopowder exhibited a typical p-type semiconducting nature, as there was a decreased in resistance across sensor on exposure to the reducing H_2S gas. When the H_2S gas was inleted, the overall reaction of H_2S and chemisorbed oxygen species as follows (Balamurugan and Lee, 2015);

$$2H_2S_{(ads)} + 3O_2{}^-{}_{(ads)} \rightarrow 2H_2O_{(g)} + 2SO_2(g) + 3e^- \quad (1)$$

$$2H_2S_{(ads)} + 4O^-{}_{(ads)} \rightarrow 2H_2O_{(g)} + 2SO_{2(g)} + 4e^- \quad (2)$$
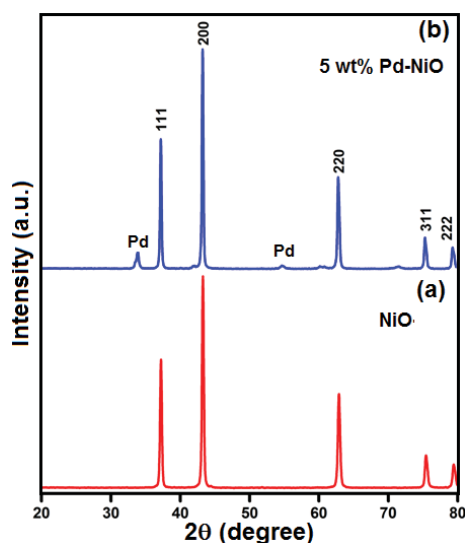
Figure 1: X-ray diffraction patterns of NiO precursor calcined at 500 °C for 2h (a) and 5 wt% Pd doped NiO nanopowder.
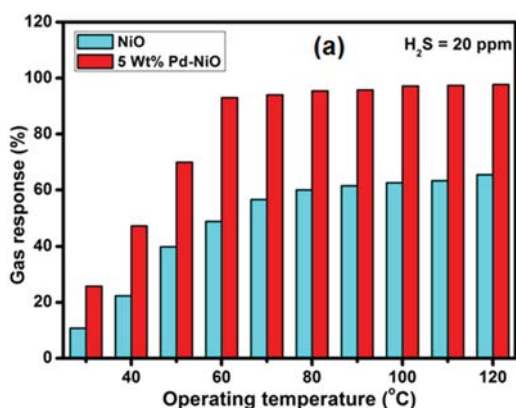

Figure 2: Response of NiO and 5 wt% Pd doped NiO based sensor to H_2S gas as a function of operating temperature.

4 CONCLUSIONS

In this work, Pd-doped NiO nanopowders have been presented as suitable semiconductor materials for selective H_2S detection. The sharp and single diffraction peaks of XRD confirm the formation of single-phase polycrystalline cubic NiO nanomaterials. The gas sensing behaviour of NiO is strongly dependent on the amount of Pd doped in NiO. The sensitivity increased with increasing Pd content and attained the maximum (93%) at 5 wt% Pd doped NiO calcined at 600 °C for 2 h.

ACKNOWLEDGEMENTS

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