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Characteristics of NiO-Doped TeO Thin Films Prepared by Pulsed-Laser Deposition

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Abstract

The influence of doping level of tellurium oxide films with different amounts of NiO additives (5, 10, 15 and 20%) on structural, optical, and electrical properties is investigated. The films were prepared by pulsed-laser deposition method. The Hall effect measurements show an increase in the conductivity with increase the NiO ratio and transfer the type of charge carriers from n to p-type with 20% NiO. The H2S sensing properties are influenced by the NiO ratio in the TeO films as well as the operation temperature. The TeO sensor loaded with 10% NiO is extremely sensitive to H2S and the best operation temperature is 50°C, and exhibits fast response speed of 7 s and recovery time of 20 s for trace level (10 ppm) H2S gas detection.

Keywords: Tellurium oxide; Thin films; Pulsed-laser deposition; Gas sensing
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1. Introduction

Tellurium-dioxide (TeO), also known as stannic oxide, is a widely used ceramic material [1]. It has a direct band-gap which width is equal to 3.6 eV [2] and high exciton binding energy of 130 meV, and excellent optical and electrical properties with outstanding chemical and physical stabilities in harsh environments [3,4]. Stoichiometric TeO is an insulator, small shifts from its perfect stoichiometry (i.e. TeO_{-x}, with x<1), or shallow doping (F or Sb) lead to n-type semi-conductive behavior of the material [5]. Its electrical conductance results from point defect such as oxygen vacancies and interstitial tellurium atoms, that acts as donor [6]. For this reason, TeO is grouped with a category of materials known as transparent conductive oxides (TCOs) which combines high electrical conductivity with optical transparency [7]. Due to their low fabrication cost, TeO thin films have a widely application such as gas sensor materials, low-emission glasses and heat mirrors, flat panel displays, touch panels, oxidation catalysts, flexible electronics, dye-sensitized solar cells (DSSCs), etc. [5-8]. TeO is considered one of the promising candidates for constructing the short wavelength optoelectronic devices, such as ultraviolet light emitting diodes (LEDs), laser diodes solar- and visible-blind photodetectors [4,9-11].

An increased concern over safety in civilian homes and industrial settings, much attention has been paid to the search for semiconductor gas sensor [12-17]. The detection and control of H_2S which is bad smelling and toxic gas is very important in laboratories and industrial areas where it is used as process gas or generated as a byproduct [16]. H_2S gas finds many applications in fields such as auto ventilation units, and medical field of dentistry [12,18].

The sensing properties of various semiconductor oxides, especially TeO-based materials, have been widely studied, which is the most preferred material for gas sensor application because of its enhanced ability to absorb oxygen on its surface and thus is highly sensitive towards many toxic and harmful gases [19]. The principle work of these sensors is a change in electrical conductance when exposure to the gas which is to be detected [20]. Desirable characteristics of a gas sensor are high sensitivity, selectivity, stability, fast response time, fast recovery time, and should be cost effective and reliable over long term [12,14,21].

The sensing properties of TeO gas sensors influence by many factors (intrinsic &extrinsic), the effective way to improve sensitivity and selectivity is modification of surface and bulk properties of tellurium oxide by doping [22]. It has been observes that the basic oxide additives promote the sensitivity and selectivity of TeO-based sensor to oxidation and reducing gases [23,24]. Nickel oxide (NiO) catalyst in TeO-based sensor is gaining a lot of importance for trace level detection of hydrogen sulfide (H_2S) gas [25]. In 1991, Maekawa et al. have presented the first report on enhanced sensitivity of TeO with

NiO dopant to detect H_2S gas [26]. Subsequently several studies showed the high sensitivity and selectivity for NiO doped TeO sensors using, thin films of tellurium oxide doped with different amount of Cu dopant [27], Cu/TeO bilayers [28], TeO-NiO-TeO sandwich structure [29], thick and thin films of TeO doped with NiO [30]. NiO does not react with TeO, therefore p-n junctions formed between p-type NiO and n-type TeO, which destroyed by formation CuS when exposure to H_2S gas [31,32].

In this work, NiO-doped TeO samples with different doping ratio were prepared by solid state reaction, which then used to fabricate film gas sensor by using pulsed laser deposition technique. The sensing characteristics of the NiO-TeO composite thin film with respect to H_2S gas were measured.

2. Experimental Details

Nickel oxide doped with different doping ratio (5, 10, 15, 20%) added to TeO powder and synthesized by solid state reaction by using NiO (99.9% Fluke) and TeO (99.5% ERAK). The two binary compounds mixed carefully for an hour and pressed at 5 ton to form a target (pellet shape with 13 mm diameter and 3 mm thickness), and then sintered in 950°C for two hours.

The NiO-doped TeO thin films have been prepared on glass and silicon substrates using pulsed laser deposition technique (PLD) with high quality using second harmonic generation (SHG) from a Nd:YAG Q-switched laser beam with a pulse width 10 ns, repetition frequency of 6 Hz and pulse energy of 400 mJ. The number of laser shots was 400 incident on the target surface with an angle of 45°. The deposition was carried out inside a vacuum chamber (10^{-2} mbar). Single crystal n-type silicon wafer substrates with phosphor doping, crystal orientation (111), thickness 508 μm and electrical resistivity of 1.5-4 Ω.cm. Square shape Si samples each of 10 mm^2 area were prepared. The films should be homogenous as possible to ensure good quality.

In order to measure the electrical properties, ohmic contacts are needed. It was obtained by evaporated Al wire of high purity under vacuum. The best condition for good ohmic contact was satisfied by a layer of 200 nm. The Hall effect measurements were carried out by using Ecopia 3000 HMS system.

Laser interferometer was used to measure the film thickness, which was in the range 200±20nm. The gas sensing properties were performed in the specially designed gas sensor test rig. The test rig was used with stainless steel cylindrical test chamber. The chamber had an inlet for the test gas to flow in and an air admittance valve. The changes in the resistance values of sensor which result from interaction with the target reducing H_2S gas with concentration 10 ppm were recorded using a data acquisition system consisting of multi-meter interfaced with a computer.

3. Result and Discussion

The type of charge carriers, conductivity, carrier concentration (n_H) and Hall mobility (μ_H), have been estimated from Hall measurements. Table (1) illustrates the main parameters estimated from Hall Effect measurements for TeO thin films deposited at room temperatures on glass substrates with different doping NiO ratio (5, 10, 15, 20%). It is clear from this table that pure and doped films with (5, 10, 15%) have a negative Hall coefficient (n-type),and change to p-type when the doping ratio increase to 20%.The conductivity increase with increasing the NiO ratio, its increase from $2.16x10^{-7}$ to $4.06x10^{-5}$ $(\Omega.cm)^{-1}$, and in general the Hall mobility (μ_H) also increase, while the carriers concentration (n_H) decrease with increasing doping ratio as shown in table (1).

Table (1) The electrical measurements of pure TeO and doped with different ratios of NiO films

Sample	Type	σ $x10^{-6}$ $(\Omega.cm)^{-1}$	n $x10^{11}$ (cm^{-3})	Mobility μ (cm/V.s)
Pure TeO	n-type	0.216	24.90	0.54
5% NiO	n-type	7.33	7.36	62.10
10% NiO	n-type	6.82	4.31	98.80
15% NiO	n- type	38.4	35.50	67.50
20% NiO	p-type	40.6	2.78	909.00

The gas sensitivity and response as well as recovery characteristics of pure TeO and NiO-doped TeO sensor elements were evaluated at room temperature, 50, 100 and 150 °C for H_2S gas to determine the optimum operating temperature of these sensors. Tellurium oxide films which prepared freshly adsorb oxygen atoms on the surface when it exposed to air. These oxygen atoms pick up the electrons from conduction band of tellurium oxide and transfer to O^- ions. So that the surface of tellurium oxide particle have negative charge, and there is a positive charge layer just below the surface particle due to depletion of electrons from donor atoms. When the TeO sensor exposed to reducing gas (H_2S) at room temperature and elevated temperature, the O^- ions on the surface react with the gas and release the

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electrons to the conduction band, as a result the depth of depletion layer decreases, this means the height of the potential barrier decreases and the resistance of sensor drops.

The sensitivity of NiO-doped TeO films to H_2S gas is increased due to the following mechanism. Due to an absence of interaction between TeO (n-type) and NiO (p-type) for sintered TeO:NiO films, the NiO grains are residing between TeO grains and forming a network of p-n junctions, that means a p-n junction forms at each interface between NiO and TeO grains. In an oxidizing atmosphere, a thick charge depletion layer is formed at the surface of TeO and this leads to a high resistance of the film in air. When the H_2S gas flows over the film, the NiO is converted into CuS which being metallic in character, the p-n junctions destroy and transformed to a metal/n-type semiconductor configuration. Since the work function of CuS is lower than that of TeO, the band is bending. This situation occurs because – at equilibrium – there is a flow of electrons from the material of lower work function (CuS) to that of higher work function (TeO). This results in the band bending downwards which facilitates the easy flow of electrons from CuS to TeO and vice versa (i.e., there is no potential barrier between them). The flow of electrons results in a decrease in the electrical resistance. When the H_2S supply is turned off, CuS gets quickly oxidized to NiO, and the p-n junctions are restored [15].

Figure (1a) shows the dynamic resistance response of TeO sensor to 10 ppm H_2S gas at R.T, 50, 100, 150°C. The characteristic behavior of the resistance of the sensors decrease when expose to H_2S gas which is typical for n-type semiconductor oxide gas sensors. The relation between the resistance and the time of exposure to H_2S gas for TeO sensors doped with 5% of NiO is represented in Fig. (1b). It is obvious that the resistance of TeO film increases when the NiO ratio increases, this occur because nickel ions can be take either substitution or interstitial positions in the TeO lattice, since the radius of Cu (0.72Å) and Sn (0.71Å) is nearly equals, so that the Cu ions will occupy the substitution position and the reaction occurs as follows:

$$CuO + \frac{1}{2}O_2 \xrightarrow{SnO_2} Cu^{+2} + 2O + 2h \qquad (1)$$

This reaction means the substitution by Cu^{+2} causes increase "*h*" the hole concentration (oxygen vacancy), which lead to decrease in the free electron (increase the depletion layer width) and finally the resistance of TeO film increases. Also it is clear from this figure that the resistance of the TeO:NiO sensors decreases when its expose to H_2S gas.

The mechanism which explains the large decreases in resistance of TeO:NiO sensors on exposure to H_2S gas was suggested earlier [33,34].

Tellurium oxide is n-type semiconductors, when nickel oxide (p-type) adds as a dopant material, there is no chemical reaction occurs between them but the two semiconductors formed numerous p-n junctions causing very high resistance of films in air. The NiO particles converted to CuS semiconductor which is a metallic in nature by exposure to H_2S as shown by following reaction:

$$CuO + H_2S \longrightarrow CuS + H_2O \qquad (2)$$

As a result, the p-n junctions are destroyed because the band bends downward and no barrier exists between CuS which has lower work function than that of TeO. Thus the resistance of the sensors in H_2S is lower than that in air. After cease the flow of H_2S gas, the CuS oxidized by the oxygen in the chamber and converted back to NiO as follows [26]:

$$CuS + \frac{3}{2}O_2 \longrightarrow CuO + SO_2 \qquad (3)$$

The conversion of the CuS to NiO is slow at low temperatures, and the rate of oxidation increases with increasing temperature. This explains why the recovery rate of the sensor is faster at high temperatures [28].

The resistance response of each sensor structure was transformed into a sensitivity value which is one of the important parameters of gas sensors, the sensitivity of the metal oxide based materials, will change with the factors influencing the surface reactions, such as chemical components, surface modification and microstructures of sensing layers, temperature and humidity [34-36]. The sensitivity (S) of the sensors can be defined as [14]:

$$S = \frac{R_a - R_g}{R_a} \qquad (4)$$

where R_a and R_g are the resistance of the sensor in fresh air and in presence of the gas, respectively

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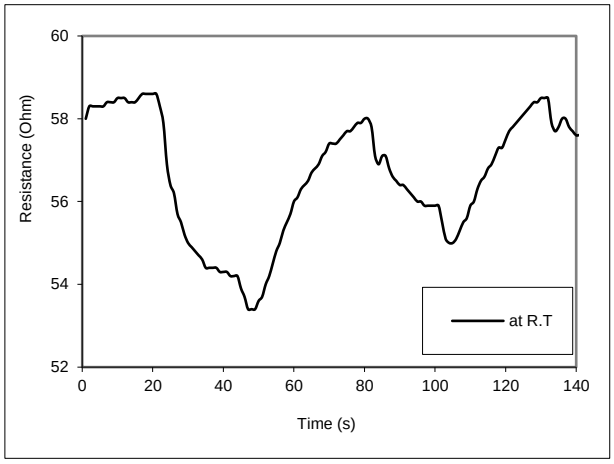

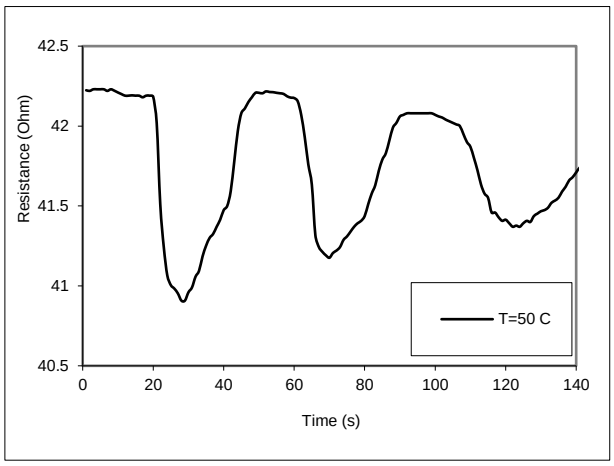

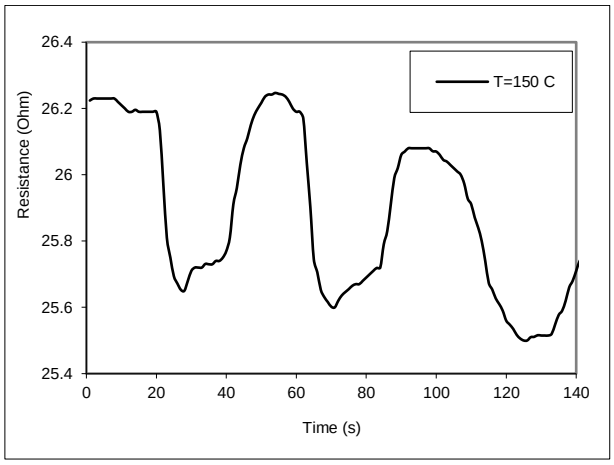

(a)

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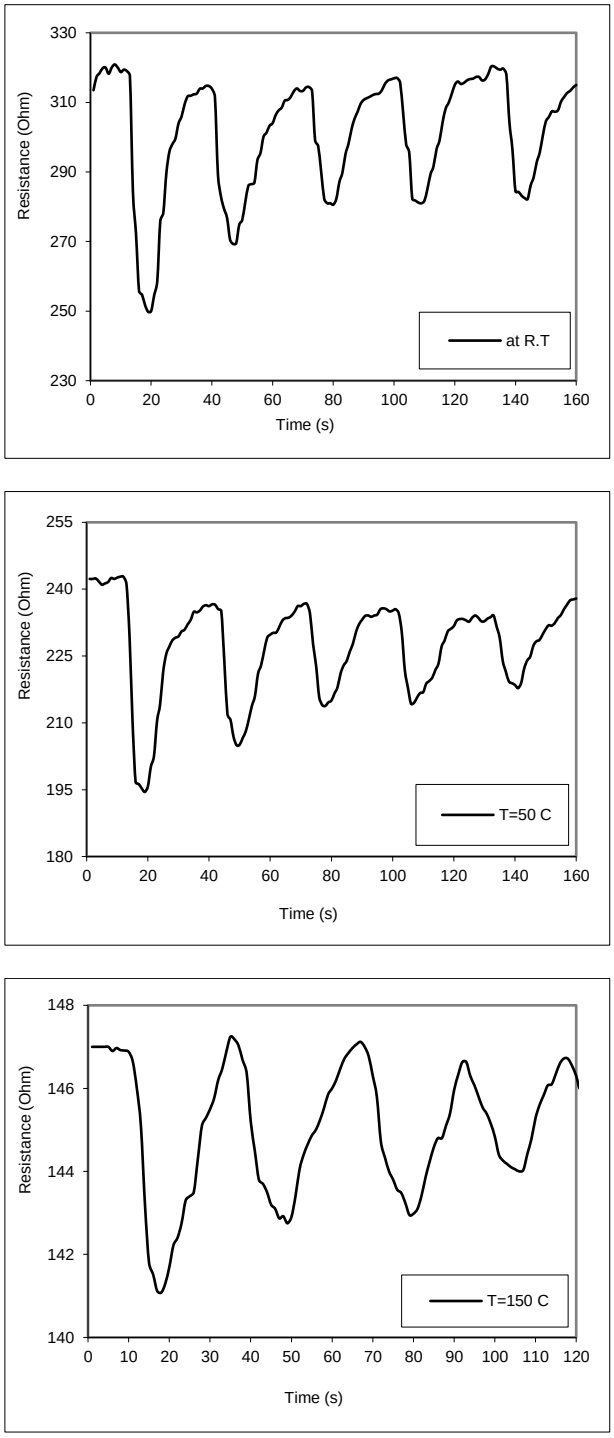


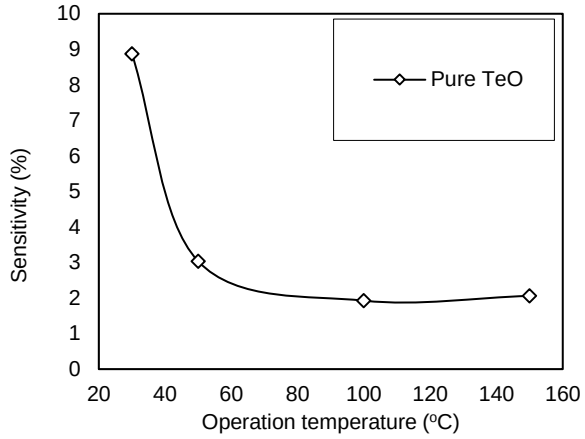
(b)

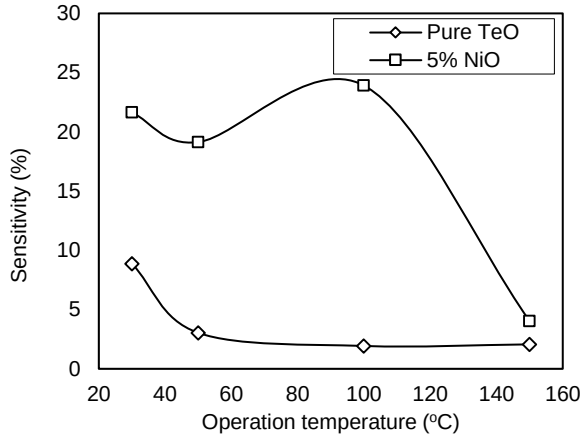
Fig. (1) The variation of resistance with time for (a) pure and (b) NiO-doped TeO films

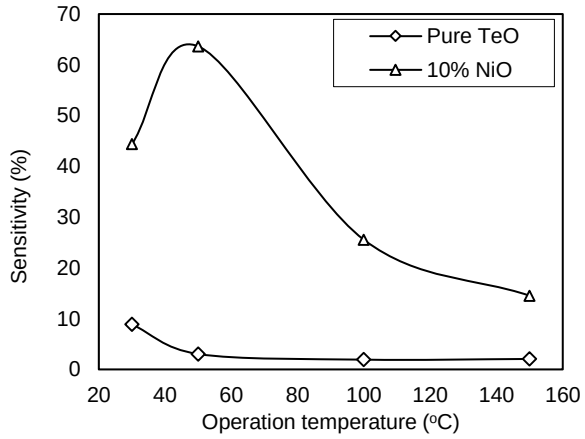
The sensitivity of the sensors against 10 ppm H_2S at different temperatures are shown in Fig. (2). It is clear from this figure that the NiO additives improve the sensitivity to H_2S gas and the maximum sensitivity recorded for the two samples which doped with 10, and 15% NiO (nano-size grains). The best operation temperature is 50°C and the sensitivity decrease with increasing temperatures. CuS is converted to Cu_2S at temperature above 103°C and the resistance of Cu_2S is higher than that of CuS and this leads to reduce the sensitivity with increasing temperature.

Detection at such low temperatures is very important to be used in chemical industries and research laboratories [28]. The sensitivity of TeO:20% NiO sensor cannot be recorded because there is a disturbance behavior for this sensor. This attributed to that the high ratio of NiO (more than 15%) the transfer of NiO to CuS does not occur completely with 10 ppm H_2S, and the modulation in the depletion

region is limited, resulting in a relatively higher value of R_g. Table (2) summarized the sensing parameters obtained for pure TeO and doped with different ratios of NiO sensors at different temperatures.







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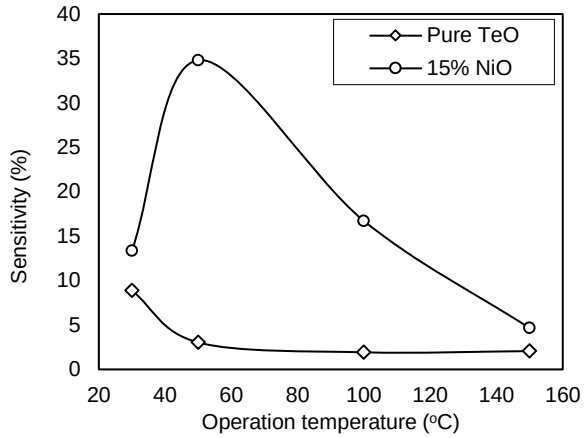

Fig. (2) (5) The variation sensitivity of the fabricated sensors with operation temperatures for different samples

Table (2) Gas sensing measurement data of pure TeO and doped with different ratios of NiO sensors at different temperatures

Materials	Temperature (°C)	Sensitivity (%)	Response time (s)	Recovery time (s)
Pure TeO	28	8.87	25.2	29
	50	3.03	8.1	20.7
	150	2.06	7.2	24.3
NiO-doped TeO (5%)	28	21.63	7.2	18.0
	50	19.63	7.0	19.8
	150	4.02	7.2	15.3
NiO-doped TeO (10%)	28	44.37	7.2	20.7
	50	63.63	7.0	16.2
	150	14.52	4.5	12.6
NiO-doped TeO (15%)	28	13.35	9.0	20.7
	50	34.80	7.2	29.7
	150	4.65	15.3	10.8

4. Conclusion

This study revealed the effect of NiO additives on structural, optical and electrical properties of TeO films deposited on glass substrates by pulsed laser deposition technique. All films are n-type, except film doped with 20% NiO has appositive hall coefficient. The NiO additives has a strong effect on the sensitivity of TeO films for trace level (10 ppm) H_2S gas detection and exhibits a fast response speed and quick recovery time. The sensors doped with 10 and 15% NiO (nano-sized grains) exhibit the maximum sensitivity at 50°C.

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