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Design and Fabrication of Nanostructure TiO_2 Doped NiO as A Gas Sensor for NO_2 Detection

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Abstract

In this paper, thin films of undoped and nickel oxide (NiO) doped titanium dioxide (TiO_2) were prepared using the chemical spray pyrolysis deposition (CSP) technique, with different concentrations of nickel oxide (NiO) in the range (3-9) wt%. The morphological, structural, electrical, and sensing properties of a gas of the prepared thin films were examined. XRD measurements showed that TiO_2 films have a polycrystalline structure. AFM analysis showed that these films have a regular structure both before and after doping . The roughness of these films decreased after adding impurities but then the opposite of that took place. The electrical and gas sensing properties of titanium dioxide was also affected after doping. The highest sensitivity value was obtained at doping concentration of 5wt% and working temperature 473ºK.

Keywords: Titanium dioxide, gas sensor, nickel oxide dopant, sensitivity.

تصميم وتصنيع التركيب النانوي TiO_2 المطعم مع NiO كمتحسس غازي لكشف غاز NO_2

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الخلاصة

في هذا البحث تم تحضير أغشية رقيقة من ثاني أكسيد التيتانيوم (TiO_2) النقي والمشوب باستخدام تقنية الترسيب الكيميائي الحراري (CSP) ، بتراكيز مختلفة من اكسيد النيكل (NiO) في مدى (3–9) wt٪. تم فحص الخصائص المورفولوجية, التركيبية ،الكهربائية وتحسسية الغاز للأغشية. اظهرت قياسات XRD ان اغشية TiO_2 تمتلك ترتيب متعدد التبلور. أظهرتحليل AFM أن هذه الأفلام لها بنية منتظمة قبل وبعد التشويب. انخفظت خشونة هذه الأغشية بعد إضافة الشوائب لكنها اظهرت سلوكا مخالفا بعد ذلك. الخصائص الكهربائية وتحسسية الغازلاغشية ثاني أكسيد التيتانيوم تاثرت ايظا بعد اضافة المادة الشائبه.اعلى قيمة تحسسية حصلت عند تركيز التطعيم 5wt% ودرجة حرارة 473ºK.

1. Introduction

Due to their low cost, ease of manufacture and use, flexibility in detecting a wide variety of toxic / flammable gases, and durability in harsh environments, semiconducting metal

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oxides (SMO) have been applied to solid state gas sensors. These sensors depend on reversible changes in electrical conductivity of gas molecules to be adsorbed/ desorbed on their surfaces [1].

Titanium dioxide (TiO_2) is one of the most common semiconductor metal oxides for the production of conductometric gas sensors, due to its non-toxic nature, chemical stability, and commercial availability at low cost, robust, and general reactivity [2,3].

TiO_2 is a semiconductor that belongs to the group of transparent oxidized semiconductors and has high transparency in the visible region, high absorption in ultraviolet radiation, and high conductivity [4].

Doping opens up the possibility of modifying the electronic structure, chemical composition, and optical properties of TiO_2 nanoparticles. A great deal of work has been made to introduce metal ion doping, such as nickel, chromium, iron, vanadium, and zinc [5].

Many efforts have been made within this area, and it was presented by Nan Zhang et al., WO_3-TiO_2 heterocyclic nanofibers (HNFs) were prepared using a simple two-step process. The mechanism that appeared in the gas stock characteristics was discussed [6]. Sheini et al. used Titanium dioxide TiO_2 to produce ceramic bodies sensitive to oxygen. Silver (Ag)-doped TiO_2 was prepared to obtained a gas sensor [7]. Eadi et al., (2017) prepared Iron (Fe) doped nanoparticles of TiO_2 for gas sensor application and photocatalytic degradation [5].

In this work, structural, morphological and electrical properties for TiO_2 pure and doped with NiO were measured and determined to prepare a gas sensor device for NO_2 gas sensitivity measurement.

2. Experiment

In this work, a undoped and doped TiO_2 were prepared with different concentrations (3-9wt%) of inorganic material NiO. All TiO_2 films were prepared with an aqueous solution of titanium (III) chloride ($TiCl_3$) and NiCl from Merck KGaA, Germany using chemical spray pyrolysis (CSP) technology. These films were fabricated with molar (0.1M) for all concentrations.

To prepare nanostructure thin films by the chemical spray pyrolysis, many parameters such as the nozzle- substrate distance, flow rate, solution deposition time, concentration and deposition temperature of the films were considered used for good. The nozzle was used to spray onto a glass substrate heated at 300°C. These thin films were annealed at 600°C for 1 hour. The thickness of the prepared thin films was measured using optical technique which was equal to 275nm.

For films, structural, morphological, electrical properties and measurements of gas sensing were studied. Sensing measurements of all films were performed on n-type silicon wafers (111) substrate and sensitivity measurement was done toward NO2 as oxidizing gas.

3. Results and discussion

Structural properties of TiO_2 films before and after adding NiO were performed by the XRD diffraction studding. The structure of as deposited thin films of TiO_2, when checked by x-ray diffraction was amorphous, thus all as deposited TiO_2 thin films, undoped and doped were annealed at 600^oC to transform the structure to polycrystalline. Figure 1 and Table 1 illustrates the XRD analysis of these materials, as it is shown pure TiO_2 has many diffraction peaks and a polycrystalline structure. This result is consistent with [8-11].

Crystal structure phase is found to be the anatase phase, this agrees with (ASTM) card no. [96-900-9087]. (101) orientation was along the plane at diffraction angle of ($2\theta = 25.2119°$) and ($d = 3.5169A°$) according to card no. [96-900-9087].

After adding different concentrations (3, 5, 7, and 9)wt% of NiO, the peaks intensity decreased. The structure was converted from polycrystalline to amorphous at 7wt% and the peaks intensity started to increase again at 9wt% percentage.

There was an increase in full width of half maximum (FWHM) to more peaks but was happened a decreased crystallite size with increased doping percentage.

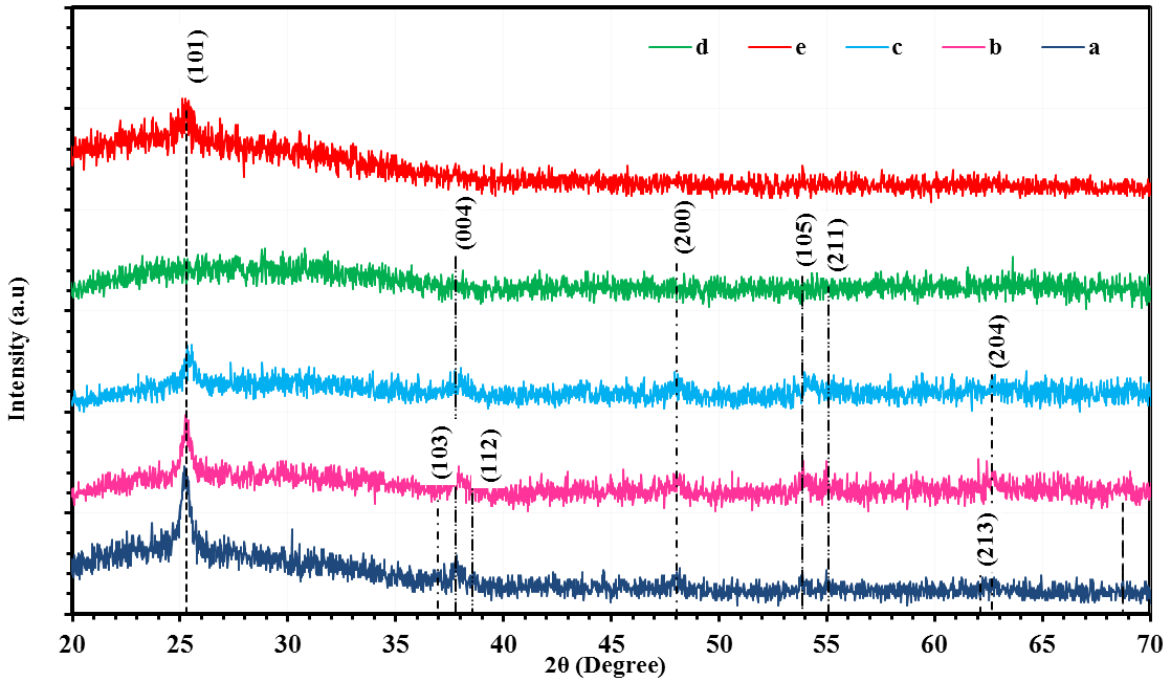

Figure 1-XRD for TiO_2 films where represents: (a) TiO_2 pure, (b) TiO_2:3%NiO, (c) TiO_2:5% NiO, (d) TiO_2:7%NiO, (e) TiO_2:9%NiO.

Table 1- The structural properties of TiO_2 samples.

NiO wt%	2θ (Deg)	FWHM (Deg)	d_{hkl} Exp.(°A)	G.S (nm)	d_{hkl} Std.(°A)	phase	hkl	Card No.
	25.211	0.572	3.529	14.211	3.516	Anatase	(101)	96-900-9087
pure	37.812	0.687	2.377	12.217	2.378	Anatase	(004)	96-900-9087
	48.006	0.744	1.893	11.679	1.892	Anatase	(200)	96-900-9087
	25.269	0.572	3.521	14.215	3.516	Anatase	(101)	96-900-9087
3	37.926	0.801	2.370	10.475	2.378	Anatase	(004)	96-900-9087
	48.064	0.687	1.891	12.655	1.892	Anatase	(200)	96-900-9087
	25.383	0.630	3.506	12.925	3.516	Anatase	(101)	96-900-9087
5	37.984	0.801	2.366	10.477	2.378	Anatase	(004)	96-900-9087
	48.064	0.801	1.891	10.848	1.892	Anatase	(200)	96-900-9087
7				Amorphous				
9	25.269	0.801	3.521	10.153	3.516	Anatase	(101)	96-900-9087

The chart of surface morphology at three dimensions for undoped and doped (with different concentrations) TiO_2 are shown in AFM images as declared in Figure 2. undoped and doped films displayed a granular structure through images of AFM. The roughness of films decreased after doping with NiO but increases at 9wt% concentration of NiO (see Table 2). Thin films with high roughness are ideal for interaction between film and gas in gas sensors and results in higher sensitivity [12]. The average diameter shows significant reduction as NiO is introduced to the host material but then the average diameter gets to grow in a non-regular manner with the increase of nickel oxide concentration.

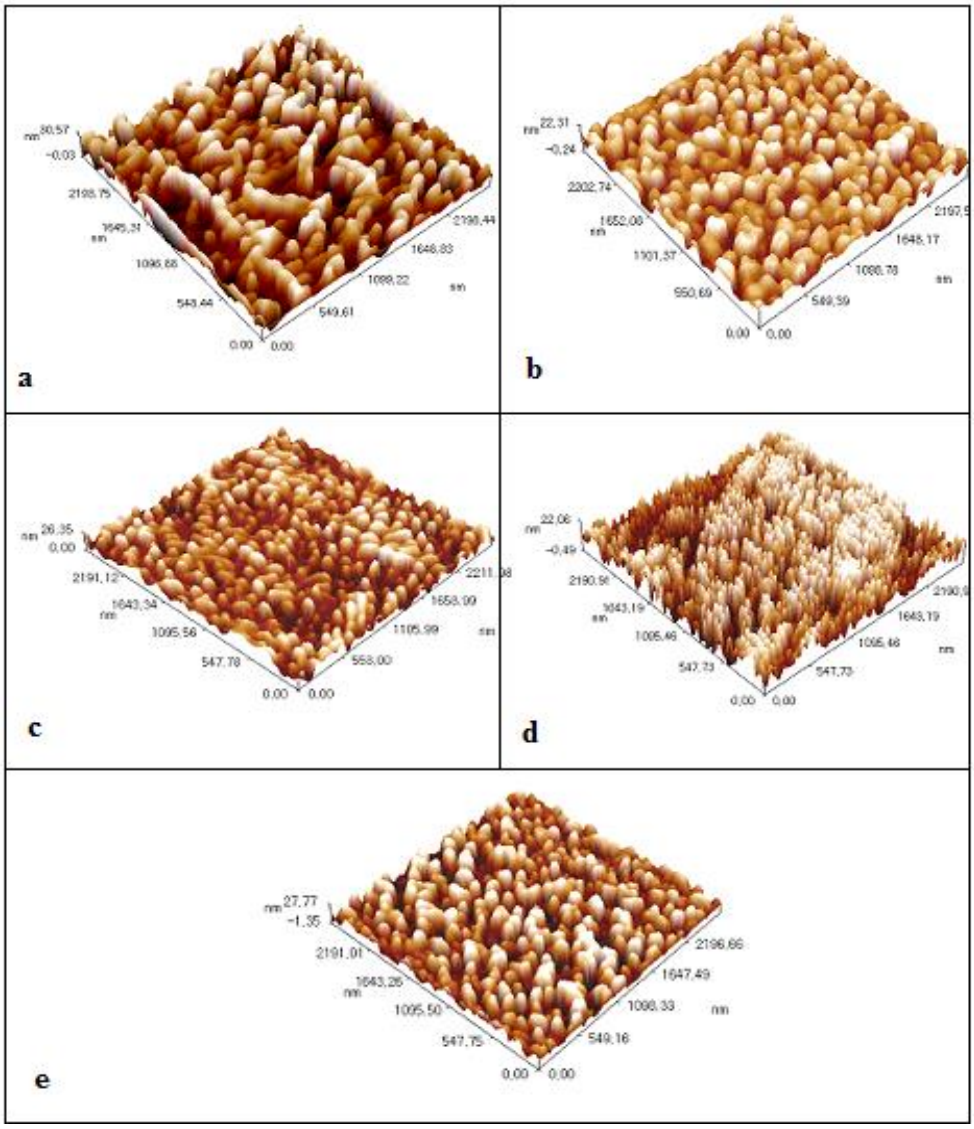

Figure-2 AFM images for TiO_2 films (a) undoped TiO_2 (b) TiO_2:3%NiO, (c) TiO_2:5%NiO, (d) TiO_2:7%NiO, (e) TiO_2:9%NiO.

Table 2- AFM parameters of TiO_2 pure and TiO_2:NiO.

NiOwt%	Roughness average (nm)	Average Diameter (nm)
0	7.65	113.97
3	3.40	76.95
5	5.08	90.00
7	5.71	62.87
9	7.28	93.98

Hall effect measurements of the undoped and NiO doped TiO_2 thin films were performed with the van der Pauw method at room temperature. Electrical properties such as free carrier concentrations **(**n_H), mobility (μ_H), Hall coefficient (R_H) and conductivity (σ_{RT}) of all anatase phase thin films nanoparticles with different concentrations are exhibited in a Table 3.

Table 3- Hall measurements parameters of TiO_2 pure and TiO_2:NiO.

NiOwt%	n_H (cm^{-3})	μ_H(cm^2/V.s)	$\sigma_{R.T}$ $(\Omega.cm)^{-1}$	R_H (m^3/C)	Carrier type
0	-1.530 E+13	1.594 E-01	3.907 E-05	-4.080 E+05	n
3	-2.951 E+12	1.742 E-01	3.237 E-05	-2.115 E+05	n
5	-1.544 E+12	1.241 E-02	2.311 E-05	-1.126 E+05	n
7	-0.540 E+12	1.296 E-02	1.917 E-05	-2.362 E+06	n
9	-1.326 E+13	1.125 E-01	2.389 E-05	-4.708 E+05	n

In this work, carrier concentrations of TiO2 films e decreased after doping with NiO but increased at 9wt% concentration of NiO. At low carrier concentrations, the grain may be seriously depleted by the free carriers due to the presence of trap states at the grain boundaries. So, the depletion region becomes very thin located at the grain boundary when the carrier concentration is sufficiently high [13].

From Table 3, it is observed that the conductivity (σR.T) is high or low according to the carrier concentration i.e. low carrier concentration results in low conductivity and visa versa.. Hall measurements resulted in negative hall coefficient for all films indicating n-type charge carriers.

The gas sensing properties have been defined as a function of operating temperature in terms of sensitivity response, response time and recovery time. Sensing properties of nanoparticles TiO_2 undoped and doped with different concentrations of NiO were studied by exposure to NiO_2 gas. This was performed as a function of time and temperature(starting at room temperature up to 473°K), as shown in Figures 3 to 7.

Figure 3 shows the sensitivity changes of pure TiO_2 thin films when exposed to NO_2 gas. Table 4 shows the sensitivity of the thin films (undoped and doped) at different working temperatures upon exposure to NO_2 gas.The highest sensitivity for the undoped TiO2 was at 423ºK. While the highest sensitivity for the doped TiO2 was for 5wt% doping concentration at 473ºK working temperature

All the undoped and doped gas sensor cells acted as n-type semiconductor since the resistance get toincrease under exposure to NO_2 oxidizing gas except for TiO_2:7%NiO/c-Si. However, gas sensor cells at working temperatures 423ºK and 473ºK acted as a p-type semiconductor since the resistance was reduced when exposed to NO_2 gas. This result is in agreement with that of Yüce and Saruhan [14].

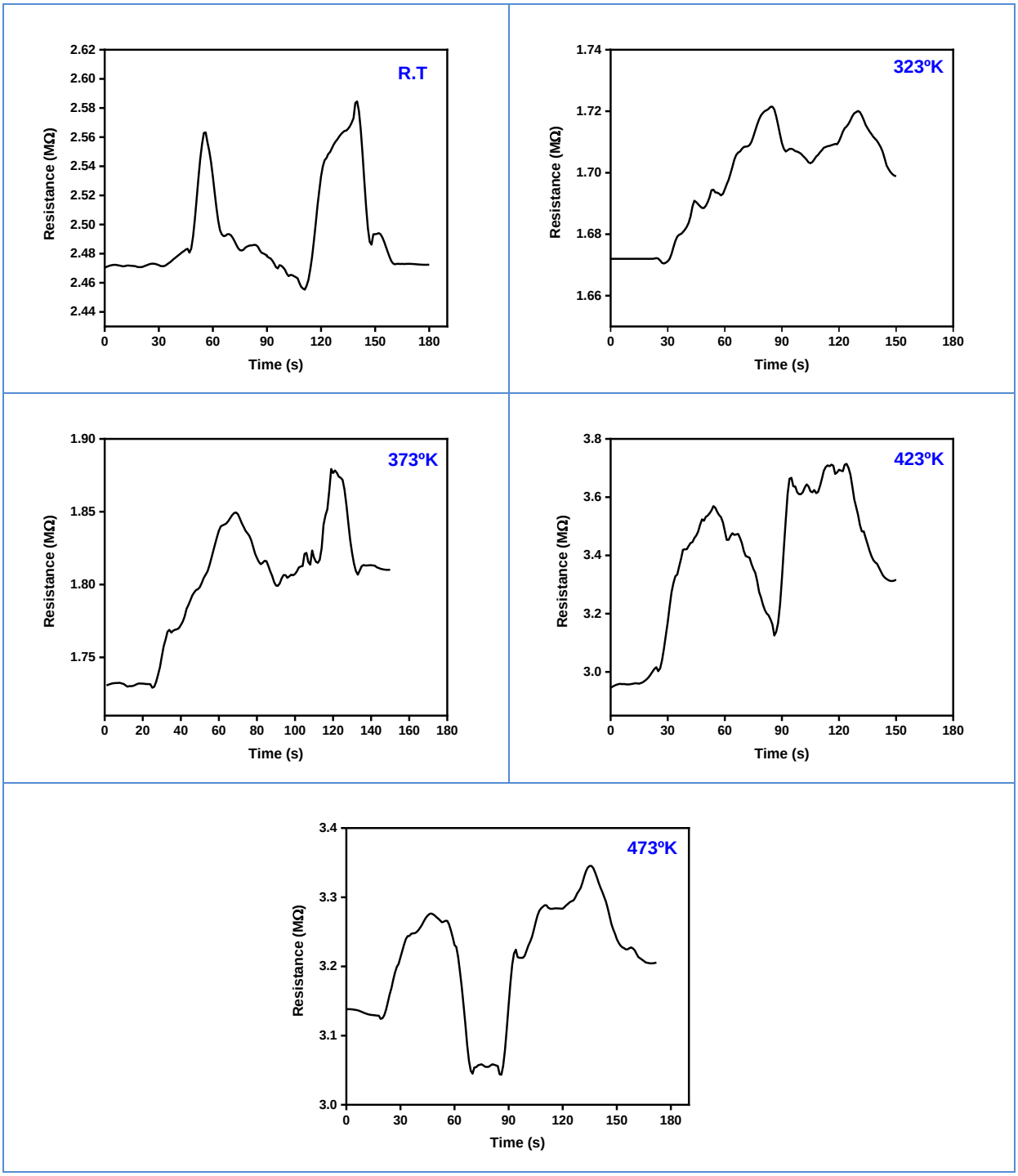

Figure 3-Variation of resistance with time for TiO_2/c-Si thin film gas sensors.

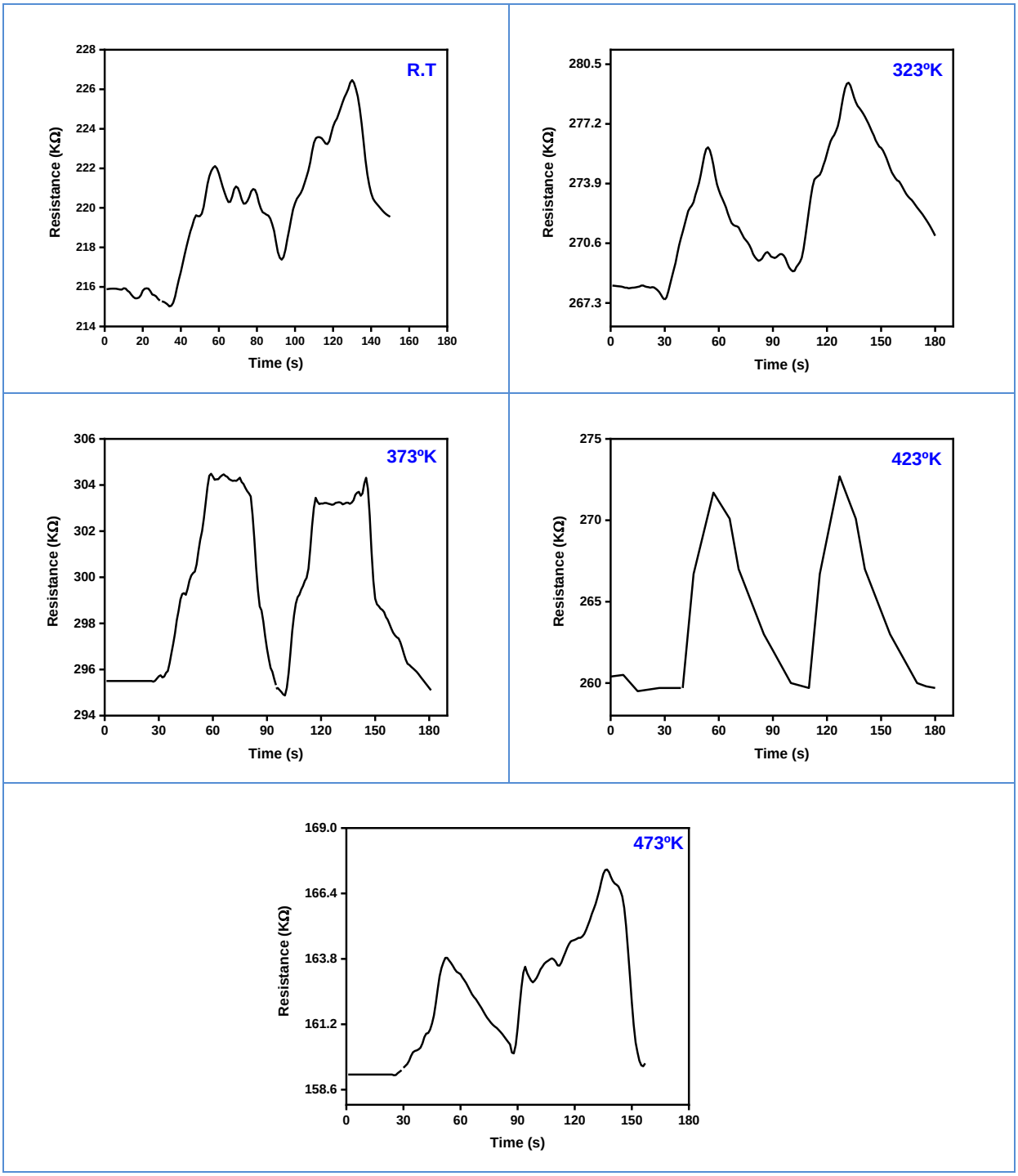

Figure 4-Variation of resistance with time for TiO_2:3%NiO/c-Si thin films gas sensors.

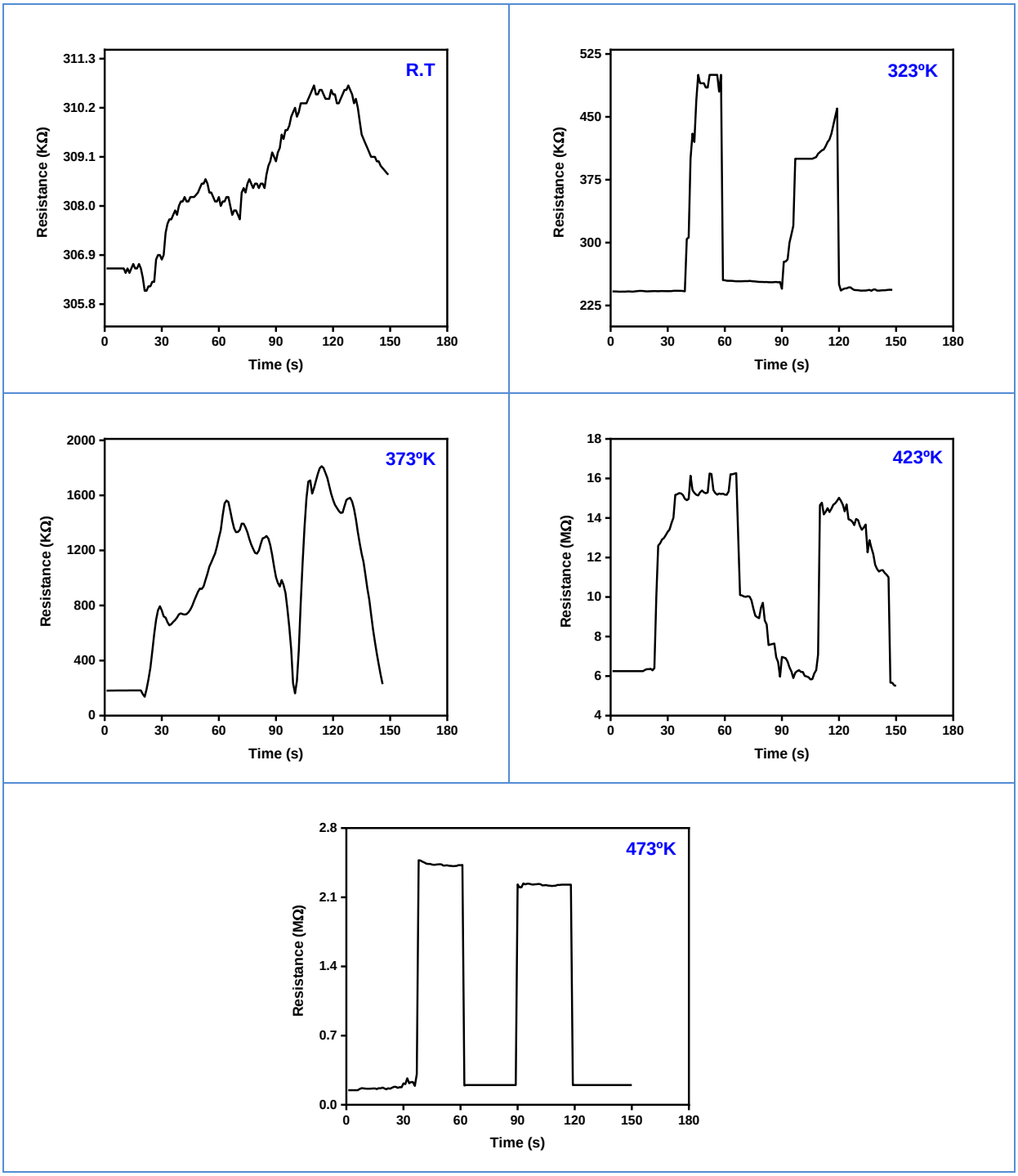

Figure 5-Variation of resistance with time for TiO_2:5%NiO/c-Si thin films gas sensors.

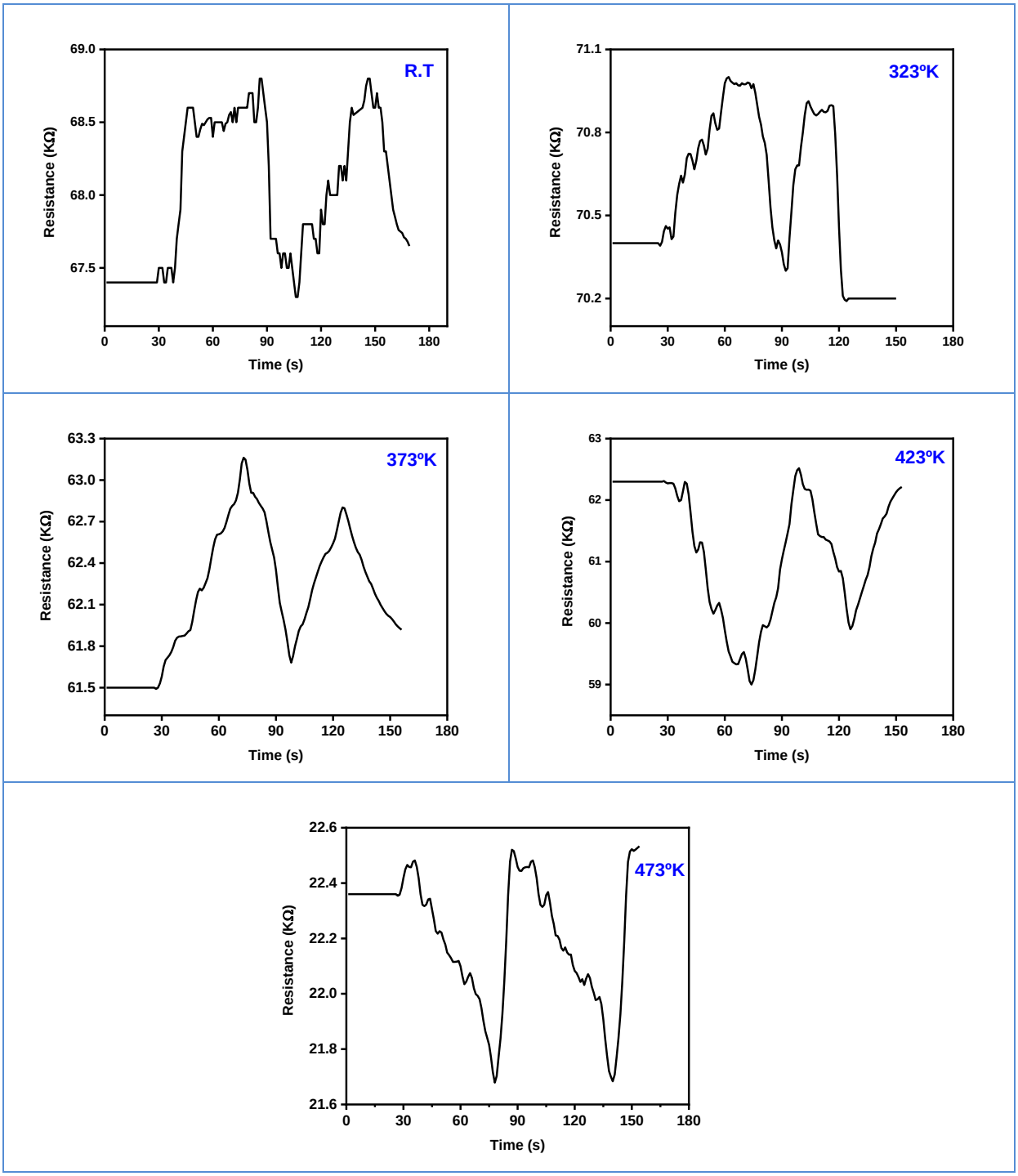

Figure 6-Variation of resistance with time for TiO_2:7%NiO/c-Si thin films gas sensors.

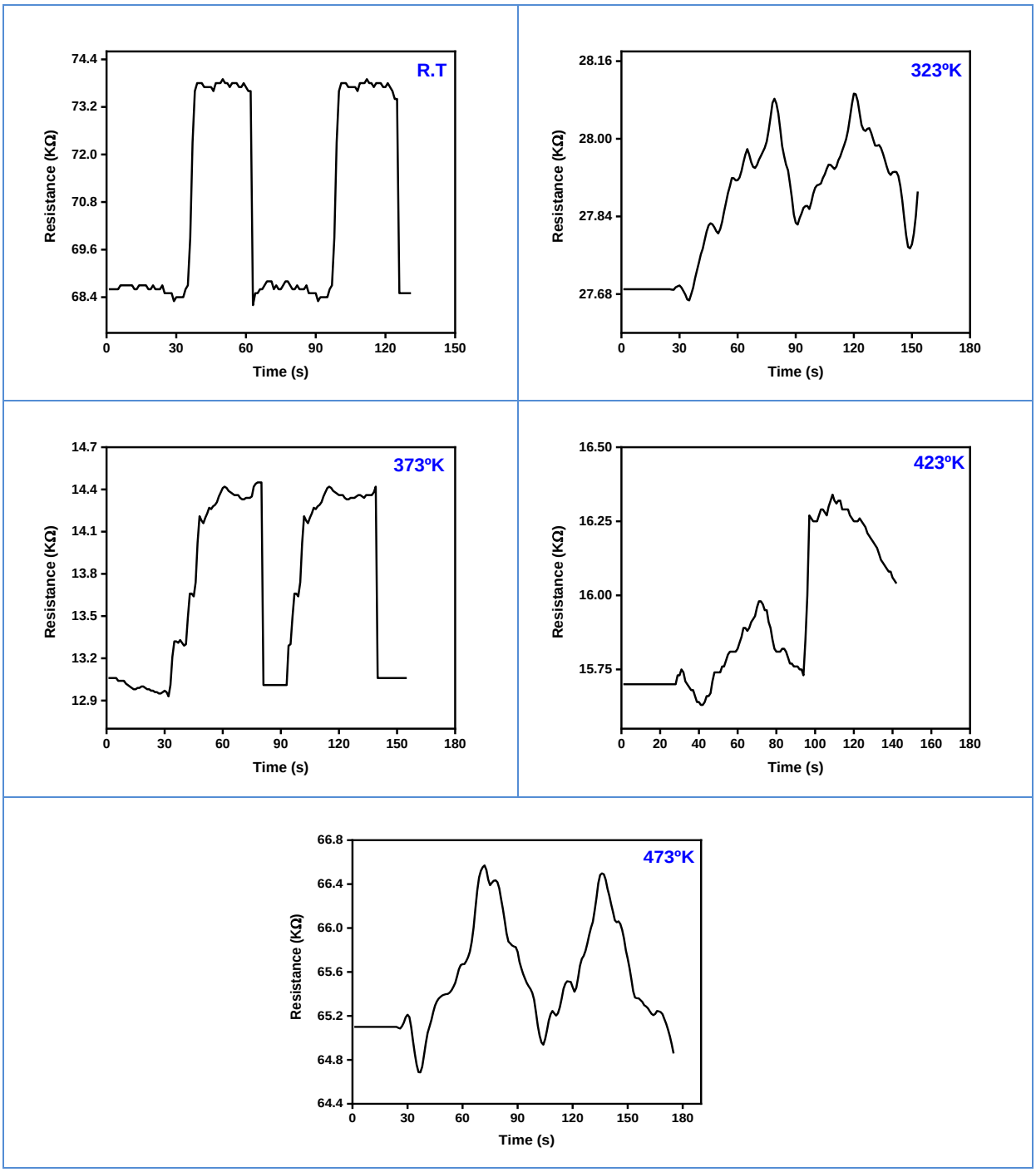

Figure 7-Variation of resistance with time for TiO_2:9%NiO/c-Si thin films gas sensors.

Table 4-Sensitivity of undoped and NiO doped TiO_2 thin films as a function of working temperature.

Operating temperature (ºK)	Sensitivity				
	NiOwt%				
	Pure	3	5	7	9
R.T	5.21	4.09	0.90	2.22	7.98
323	3.17	3.89	106.18	0.86	1.51
373	6.75	2.97	780.28	2.78	11.75
423	18.56	5.00	158.70	5.43	3.81
473	9.76	4.53	1103.88	3.73	3.04

The response time values as a function of temperature of pure and doped samples increased but in a non-regular manner with the rising of working temperature except for theTiO_2: 5%NiO/c-Si sample i.e. the response time was reduced.(as shown in Table 5).
The recovery time of (pure, 3 and 9)wt.% increased by rising of working temperature while the recovery time gets to reduce by rising of working temperature for residual gas sensors cells i.e.TiO_2:5% and 7% NiO/c-Si.

Table 5- Response and recovery time of undoped and NiO doped TiO_2 thin films as a function of working temperature.

Operating temperature (^{o}K)	Response time(sec)					Recovery time (sec)				
	NiOwt%									
	Pure	3	5	7	9	Pure	3	5	7	9
R.T	15.92	31.50	36	34.38	7.41	19.86	13.5	16.11	16.97	1.47
323	43.09	28.59	7.20	25.34	39.42	5.293	37.92	1.21	11.62	9.66
373	27.55	22.50	1.77	39.34	22.68	18.55	17.10	12.51	14.26	1.40
423	18.03	14.13	11.57	29.74	11.34	25.91	37.20	19.53	13.49	19.14
473	37.14	41.90	1.91	37.19	30.76	25.85	14.46	1.87	5.53	19.61

4. Conclusions

Polycrystalline structure of TiO_2 , undoped and doped with NiO up to 9wt%, was obtained using chemical spray pyrolysis technique subjected to annealing at 600^{o}C for one hour. Further increase of doping ratio leads to amorphous thin films. The degree of crystallinity as well as crystal size were growing with a further increase of doping ratio. The grain size as measured by from AFM affirms the same results. The charge carriers concentration as well as the conductivity was reduced by the addition of NiO to the host oxide in the first stage and then increased. The mobility exhibit to change in opposite to that. Maximum sensitivity obtained needs relative high adsorption sites which are provided from moderate crystal size and good surface roughness.

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