

PAPER • OPEN ACCESS

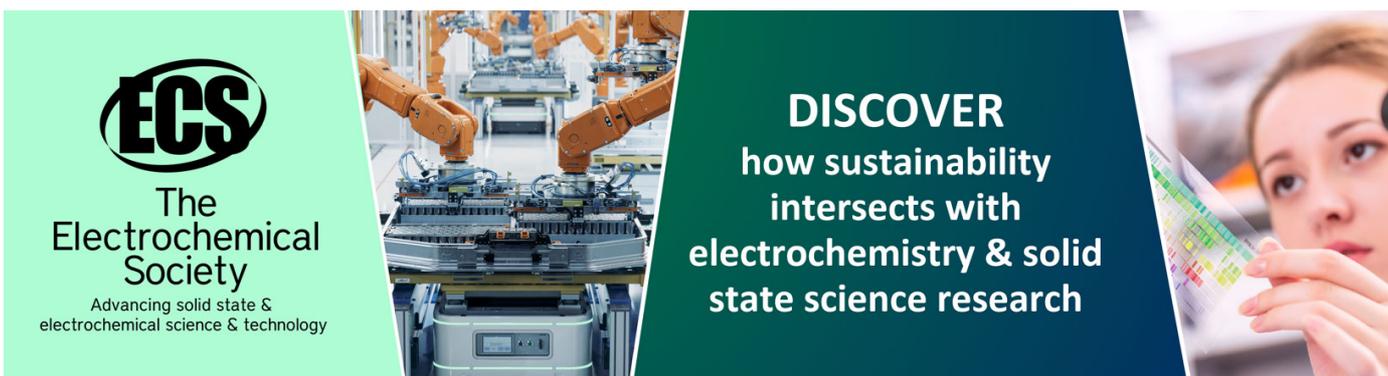
Tin Oxide Microheater for Chemical Sensors

To cite this article: Mohsen Gharezi and Mohammad Ansari 2016 *IOP Conf. Ser.: Mater. Sci. Eng.*
108 012018

View the [article online](#) for updates and enhancements.

You may also like

- [Low-power catalytic gas sensing using highly stable silicon carbide microheaters](#)
Anna Harley-Trochimczyk, Ameya Rao, Hu Long et al.
- [Critical analysis of micro-thermogravimetry of \$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\$ crystals using heatable microcantilevers](#)
Nikhilendu Tiwary, Marjan Zakerin, Filipe Natalio et al.
- [Thermally/mechanically robust anodic aluminum oxide \(AAO\) microheater platform for low power chemoresistive gas sensor](#)
Byeongju Lee, Incheol Cho, Mingu Kang et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Tin Oxide Microheater for Chemical Sensors

Mohsen Gharezi^{1a} and Mohammad Ansari^{1b}

¹Electronic Materials Laboratory, Electrical Engineering Department, K.N. Toosi University of Technology, Tehran 16317-14191, Iran.

^amohsengharezi@ee.kntu.ac.ir, ^bmohammad.ansari1371@gmail.com

Abstract. Tin oxide is the main material utilized for the fabrication of chemical sensing pellets which operate at elevated temperatures. The heating is commonly carried out with ruthenium dioxide resistors. Here, a tin oxide-based microheater is developed for microsensor applications. These microheaters are fabricated on 0.5 mm thick alumina substrates using spray pyrolysis technique. The optimum SnO₂ heaters have a sheet resistivity in the 40-70 Ω/\square range. Ohmic Ag/SnO₂ contacts are formed by silver paste printing followed by an appropriate thermal annealing, which provide connections to the external circuitry. Durability tests are carried out on several samples; the long-term performance of the fabricated devices is satisfactory. The method allows the elimination of the expensive ruthenium dioxide from the structure of generic gas sensors.

Keywords: Tin oxide, Microheater, Gas sensor, Thin film, Spray pyrolysis.

1. Introduction

Owing to vast applications in the fields of food safety, health care, environmental science, and many others, gas analysis is gaining importance. Gas sensors are simple, cheap, and fast tools used for quantitative and qualitative assessment of contaminants in different atmospheres. Today, analysis of simple and complex odors is possible using a single generic gas sensor [1-5]. Metal oxides are the class of materials which have been vastly used as sensing element of gas sensors [6-9]. Precious properties such as high thermal stability, wide variety of materials with different chemical, physical and optical properties, low fabrication cost, and the ability to function in harsh environmental conditions, have led to widespread applications of metal oxides in the fields of optoelectronics and chemical sensors [10-12]. The role of metal oxides in sensor technology is not limited to being used as the sensing element; they have also been successfully used as electrodes and heaters [13-15].

Establishing ohmic contacts to metal oxides is an unavoidable necessity in fabricating various electronic and ionic devices. Metal/metal oxide contacts have been vastly studied in recent years and these studies have led to innovative methods for forming contacts of ohmic quality to these materials [16-20]. Schottky contacts are of remarkable importance in device fabrication technology. It's been reported that Schottky-type metal/metal oxide contacts are more suitable for gas sensor applications due to their enhanced sensitivity [21-24].

In order to achieve high levels of sensitivity and short response times, the majority of gas sensors operate at elevated temperatures; so the presence of a heater in such devices is unavoidable. Durability, temperature uniformity, and the fabrication cost are the parameters which should be considered in choosing the proper heater for gas sensors. Wire heaters made of Ni-Cr alloy are common in



experimental gas sensors; although, temperature non-uniformity and relatively high power consumption are the problems which these kind of heaters face. Platinum films are also utilized as heating element of gas sensors. In order to obtain appropriate heater resistance, these films should be deposited in the shape of meanders which causes difficulties in the fabrication of the devices which are very small in size. Furthermore, catalytic interaction of gas molecules with platinum heaters can cause instabilities in sensor response [25]. Ruthenium dioxide resistors are the most common kind of heaters that can be paste printed or sputtered on sensors substrate. RuO_2 resistance has negligible dependence on temperature, but this kind of heater has some problems with its stability [26]. For example, it has been shown that ruthenium dioxide tends to reduce to ruthenium in hydrogen atmosphere at temperatures between 150 and 250°C [27].

In sensor technology, tin oxide has been vastly used for the fabrication of chemical sensing pellets. Here, a tin oxide microheater for chemical sensors is proposed. Since the microheater and the sensing pellet can be deposited using the same technique, the fabrication cost of the gas sensor decreases significantly. In this research work, tin oxide thin films are produced using a homemade spray pyrolysis deposition system. Ohmic Ag/SnO_2 contacts provide connection to the external circuitry. Durability and the microstructure of the deposited heaters are investigated.

2. Experimental

Tin oxide layers are deposited on 5 mm × 5 mm × 0.5 mm alumina substrates. The schematic diagram of the ultrasonic spray pyrolysis system utilized for the deposition of SnO_2 layers is shown in figure 1. Alumina substrates are washed with acetone (96% v/v), rinsed with deionized water, and dried on a hot plate at 150°C. The precursor is 0.1 M solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck, 107815) in absolute ethanol. Aerosol droplets, generated from the precursor using a piezoelectric transducer (900 kHz), are transported by air as a carrier gas with a flow rate of 0.1 lit/min to the deposition chamber. The piezoelectric source is separated from the precursor container by a thin polymer sheet and maintained in a water filled tank in order to prevent its precursor caused corrosion [28]. The aerosol strikes the substrate surface heated to 450°C where film deposition occurs. The surface temperature is provided using a Ni-Cr alloy wire heater embedded under the substrate and monitored using a fine S-type thermocouple. It takes about an hour to produce layers with sheet resistivity in the range of 50 Ω/\square . The samples are annealed at 700°C in air to achieve stable heater resistance.

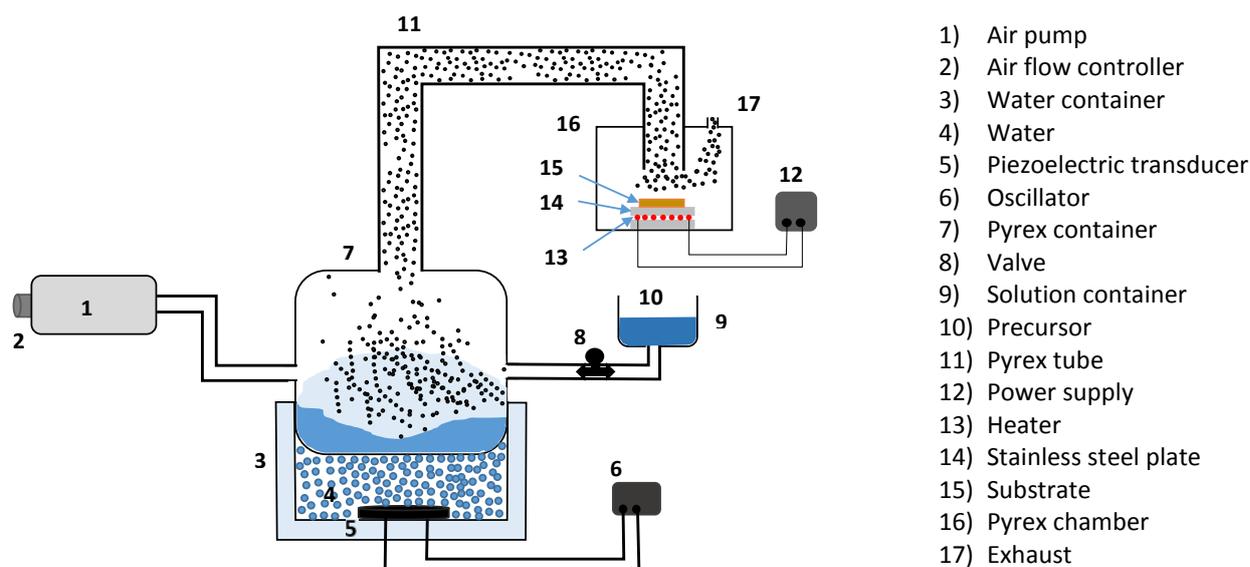


Figure 1. The schematic diagram of the homemade spray pyrolysis system used for tin oxide layer deposition on alumina substrates.

Two parallel silver electrodes are deposited on tin oxide layer utilizing silver paste printing. Fine Ni-Cr alloy wires attached to the deposited silver layers provide connection to the external circuitry. The forward biased device is heat treated at 200°C for 10 minutes to achieve ohmic Ag contacts [16]. Figure 2.a shows the schematic diagram of the fabricated sample. A fine S-type thermocouple is used for continuous monitoring of the temperature on the device surface. Temperature measurements are carried out with an accuracy of $\pm 1^\circ\text{C}$. Electronic properties of the device are investigated using a two point probe measurement system. Figure 2.b shows the experimental setup used for these measurements.

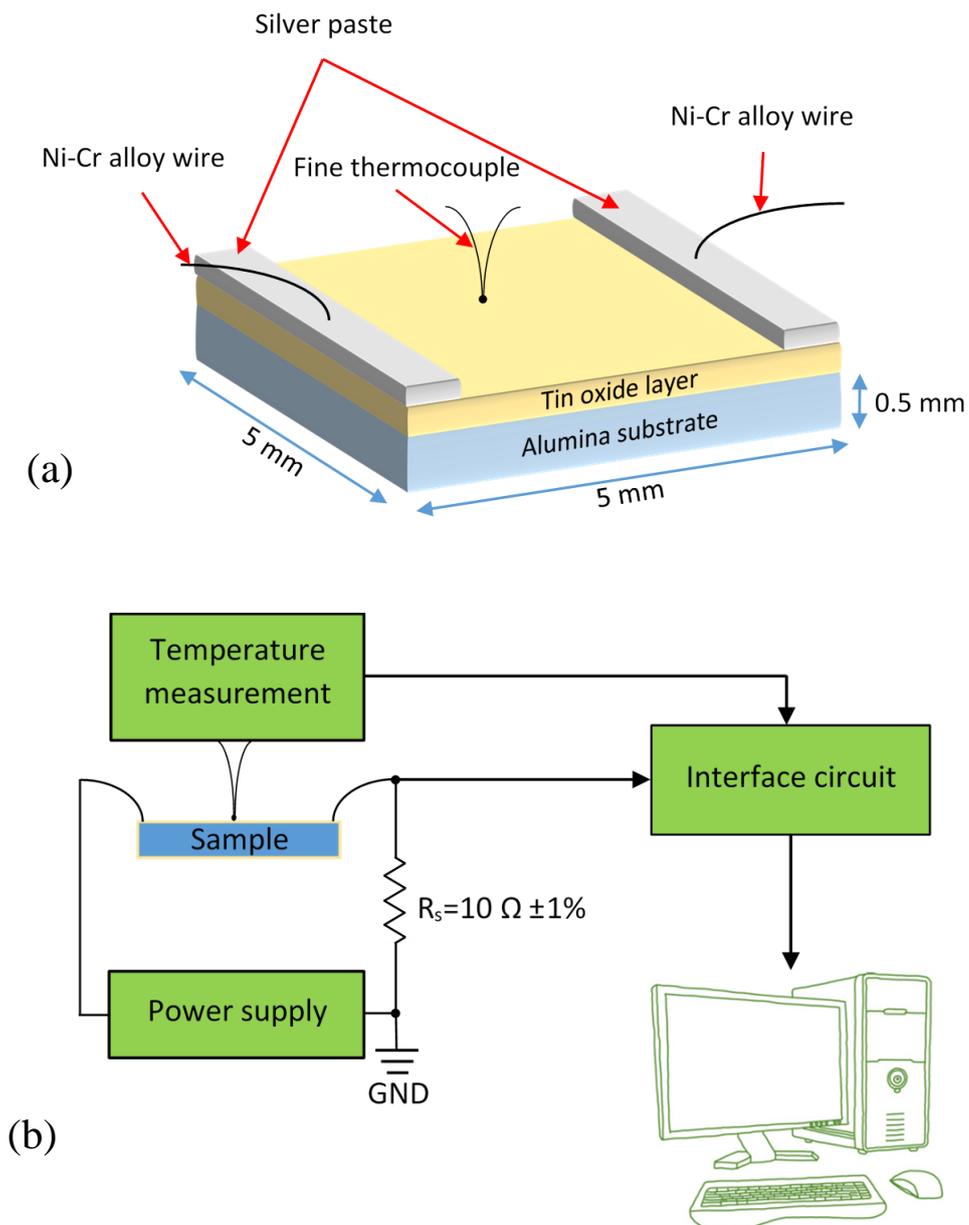


Figure 2. (a) The schematic presentation of the fabricated sample and (b) the experimental setup used for electrical measurements.

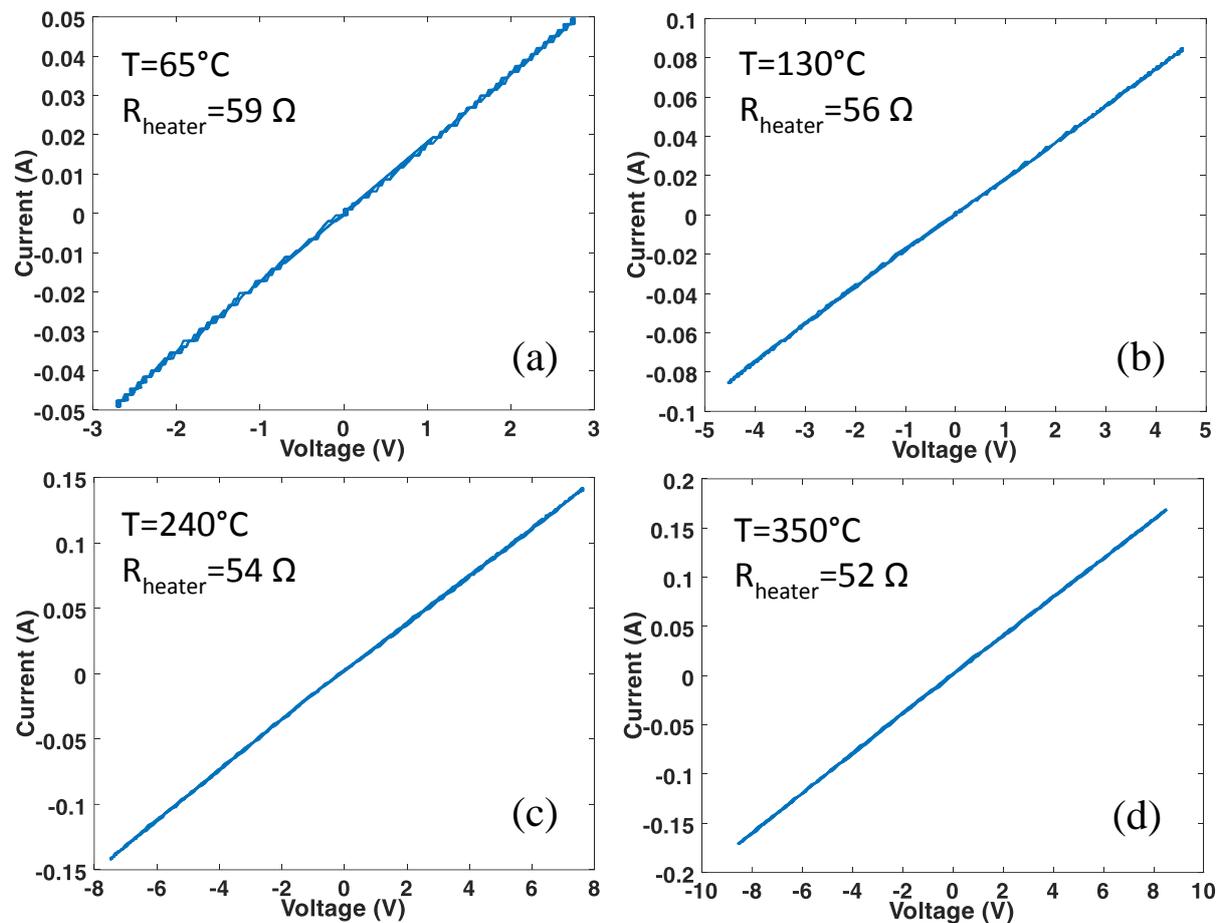


Figure 3. I-V diagrams for a heater sample at (a) $T=65^{\circ}\text{C}$, (b) $T=130^{\circ}\text{C}$, (c) $T=240^{\circ}\text{C}$, and (d) $T=350^{\circ}\text{C}$. Heater resistances are obtained using the slope of the diagrams.

3. Results

Sinusoidal waveforms with different amplitudes are applied to the fabricated sample and the resulting I-V characteristics are recorded at four different temperatures (figure 3). Linear I-V diagrams show that Ag-SnO₂ contacts are ohmic at operating temperatures in the 65-350°C range. Using the slope of the I-V diagrams, heater resistances are calculated. It can be seen that resistance variation of SnO₂ heater is only about 10% in a 300°C temperature change. For comparison, the resistance of a platinum heater doubles when it's operating at temperatures in 350-400°C range [25].

The effect of thermal annealing has been investigated by recording heater resistance of annealed and not-annealed devices continuously operating at 350°C for 2 weeks (figure 4.a). It's obvious that no significant change occurs in the resistance of the device which has been annealed at 700°C for 30 minutes; while for the not-annealed device, the resistance experiences an increase of 44% in the first 6 days and then reaches its stable value. This change can be expressed by an exponential function of time with a time constant of 1.3 days (figure 4.b). Durability tests have been carried out for different samples continuously operating at 350°C in a 1-month time period. The heater resistance remained almost unchanged in this period and only a 2% fluctuation was observed in the measured values which can be caused by the measurement errors.

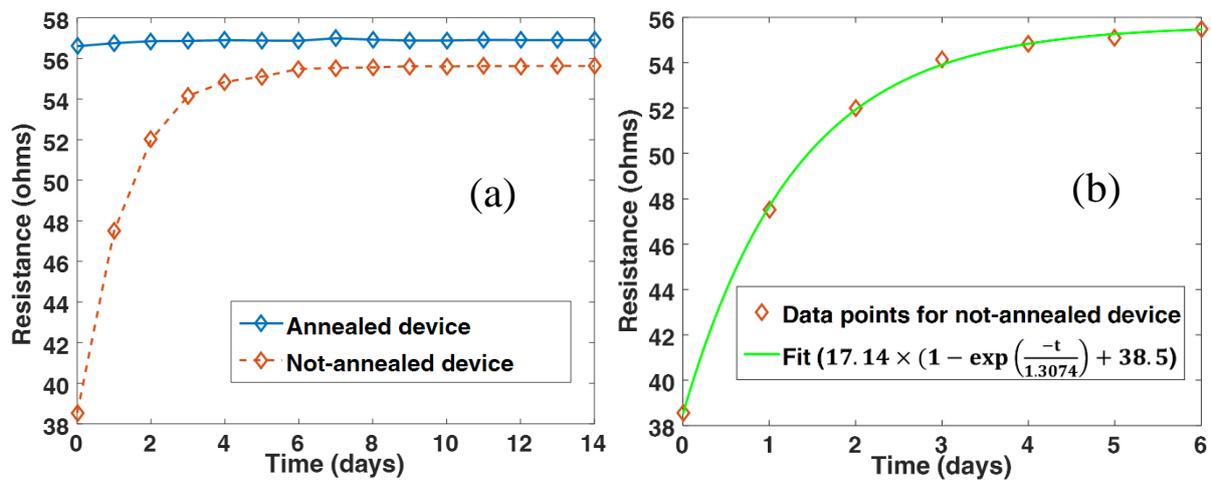


Figure 4. (a) Heater resistance of annealed (solid line) and not-annealed (dashed line) samples for a 2-week time period and (b) data points of the not-annealed device for the first 6 days and the exponential function which fits them.

The SEM micrograph obtained from the tin oxide layer surface is shown in figure 5. Roughness of the polycrystalline SnO₂ layer is obvious from the figure. The deposited layer has particles with an average size of about 500 nm, while the aggregated particles have much smaller size (~50 nm). The crystalline SnO₂ particles show a pyramidal habit which is in agreement with the reported results [29, 30].

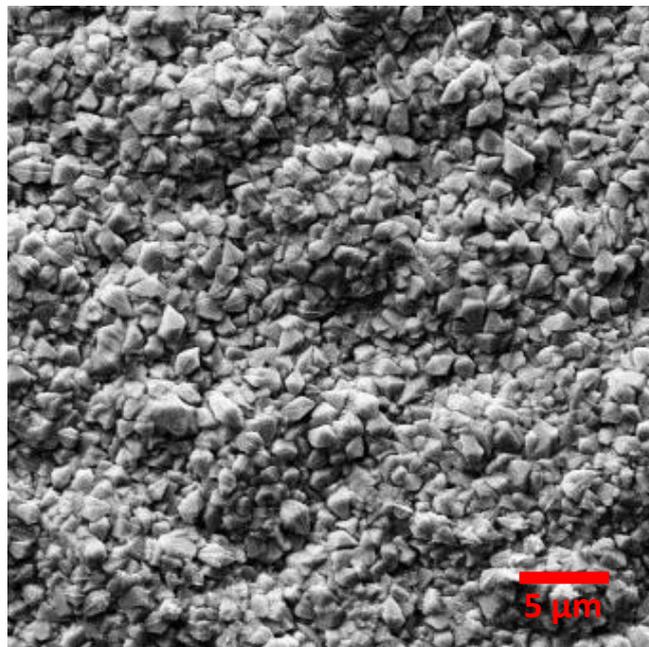


Figure 5. SEM micrograph of the SnO₂ layer surface.

4. Conclusion

A tin oxide-based microheater was fabricated using a homemade ultrasonic spray pyrolysis system. The I-V characteristics of the device at different temperatures were studied and it was shown that the formed Ag/SnO₂ contacts are ohmic in a wide range of operating temperatures. It was shown that the thermally annealed heaters are stable over time. The microstructure of the deposited tin oxide layer was investigated and it was seen that the layer has a polycrystalline structure with an average crystallite size of 500 nm and pyramidal habit. Owing to its negligible characteristics dependence on temperature, and durability, the proposed microheater can effectively function in chemical sensors. Furthermore, this microheater enables the fabrication of gas sensors sensing pellets and microheaters with the same technology reducing the fabrication cost.

References

- [1] Hossein-Babaei, Faramarz, and Amir Amini. "A breakthrough in gas diagnosis with a temperature-modulated generic metal oxide gas sensor." *Sensors and Actuators B: Chemical* 166 (2012): 419-425.
- [2] Gosangi, Rakesh, and Ricardo Gutierrez-Osuna. "Active temperature modulation of metal-oxide sensors for quantitative analysis of gas mixtures." *Sensors and Actuators B: Chemical* 185 (2013): 201-210.
- [3] Hossein-Babaei, Faramarz, Mohammad Paknahad, and Vahid Ghafarinia. "A miniature gas analyzer made by integrating a chemoresistor with a microchannel." *Lab on a Chip* 12.10 (2012): 1874-1880.
- [4] Martinelli, Eugenio, et al. "Self-adapted temperature modulation in metal-oxide semiconductor gas sensors." *Sensors and Actuators B: Chemical* 161.1 (2012): 534-541.
- [5] Hossein-Babaei, Faramarz, and Amir Amini. "Recognition of complex odors with a single generic tin oxide gas sensor." *Sensors and Actuators B: Chemical* 194 (2014): 156-163.
- [6] Wetchakun, K., et al. "Semiconducting metal oxides as sensors for environmentally hazardous gases." *Sensors and Actuators B: Chemical* 160.1 (2011): 580-591.
- [7] Miller, Derek R., Sheikh A. Akbar, and Patricia A. Morris. "Nanoscale metal oxide-based heterojunctions for gas sensing: a review." *Sensors and Actuators B: Chemical* 204 (2014): 250-272.
- [8] Kim, Il-Doo, and Avner Rothschild. "Nanostructured metal oxide gas sensors prepared by electrospinning." *Polymers for Advanced Technologies* 22.3 (2011): 318-325.
- [9] Kim, Hyo-Joong, and Jong-Heun Lee. "Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview." *Sensors and Actuators B: Chemical* 192 (2014): 607-627.
- [10] Clavero, César. "Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices." *Nature Photonics* 8.2 (2014): 95-103.
- [11] Hossein-Babaei, Faramarz, Mehdi Mohamadzade Lajvardi, and Farhad Akbari Boroumand. "Large area Ag-TiO₂ UV radiation sensor fabricated on a thermally oxidized titanium chip." *Sensors and Actuators A: Physical* 173.1 (2012): 116-121.
- [12] Comini, Elisabetta, et al. "Metal oxide nanoscience and nanotechnology for chemical sensors." *Sensors and Actuators B: Chemical* 179 (2013): 3-20.
- [13] Zhu, Lina, Yangong Zheng, and Jiawen Jian. "Effect of palladium oxide electrode on potentiometric sensor response to carbon monoxide." *Ionics*(2015): 1-8.
- [14] Chen, Xin, Xiaoyu Cheng, and J. Justin Gooding. "Detection of trace nitroaromatic isomers using indium tin oxide electrodes modified using β -cyclodextrin and silver nanoparticles." *Analytical chemistry* 84.20 (2012): 8557-8563.
- [15] Bai, Zikui, Aihua Wang, and Changsheng Xie. "Laser grooving of Al₂O₃ plate by a pulsed Nd: YAG laser: characteristics and application to the manufacture of gas sensors array heater." *Materials Science and Engineering: A* 435 (2006): 418-424.
- [16] Hossein-Babaei, Faramarz, Saeed Moghadam, and Saeed Masoumi. "Forming ohmic Ag/SnO₂ contacts." *Materials Letters* 141 (2015): 141-144.

- [17] Greiner, Mark T., et al. "Metal/Metal-Oxide Interfaces: How Metal Contacts Affect the Work Function and Band Structure of MoO₃." *Advanced Functional Materials* 23.2 (2013): 215-226.
- [18] Hossein-Babaei, F., Mehdi M. Lajvardi, and Navid Alaei-Sheini. "The energy barrier at noble metal/TiO₂ junctions." *Applied Physics Letters* 106.8 (2015): 083503.
- [19] Lee, Jeong Eun, et al. "Thermal stability of metal Ohmic contacts in indium gallium zinc oxide transistors using a graphene barrier layer." *Applied Physics Letters* 102.11 (2013): 113112.
- [20] Hossein-Babaei, Faramarz, and Mohammad Orvatinia. "Thickness dependence of sensitivity in thin film tin oxide gas sensors deposited by vapor pyrolysis." *International Journal of Engineering Transaction B: Applications* 16.1 (2003): 33-40.
- [21] Wei, Te-Yu, et al. "Gigantic enhancement in sensitivity using Schottky contacted nanowire nanosensor." *Journal of the American Chemical Society* 131.48 (2009): 17690-17695.
- [22] Hossein-Babaei, F., and S. Rahbarpour. "Separate assessment of chemoresistivity and Schottky-type gas sensitivity in M-metal oxide-M' structures." *Sensors and Actuators B: Chemical* 160.1 (2011): 174-180.
- [23] Hu, Youfan, et al. "Supersensitive, Fast-Response Nanowire Sensors by Using Schottky Contacts." *Advanced Materials* 22.30 (2010): 3327-3332.
- [24] Hossein-Babaei, F., and S. Rahbarpour. "Titanium and silver contacts on thermally oxidized titanium chip: electrical and gas sensing properties." *Solid-State Electronics* 56.1 (2011): 185-190.
- [25] Korotcenkov, Ghenadii. *Handbook of Gas Sensor Materials: Properties, Advantages and Shortcomings for Applications Volume 1: Conventional Approaches*. Springer Science & Business Media, 2013. 266-267.
- [26] Jelenkovic, Emil V., et al. "Degradation of RuO₂ thin films in hydrogen atmosphere at temperatures between 150 and 250°C." *Microelectronics Reliability* 43.1 (2003): 49-55.
- [27] Kaga, Yukinao, et al. "Thermal stability of RuO₂ thin films and effects of annealing ambient on their reduction process." *Japanese journal of applied physics* 38.6R (1999): 3689.
- [28] Moghadam, Saeed, Sepideh Zendehtell, and Ahmad Rouhollahi. "Sensitivity enhancement in SnO₂ based gas sensors by surface decoration with platinum nanoparticles." *Electrical Engineering (ICEE), 2014 22nd Iranian Conference on*. IEEE, 2014.
- [29] Brinzari, V., et al. "Morphological rank of nano-scale tin dioxide films deposited by spray pyrolysis from SnCl₄·5H₂O water solution." *Thin Solid Films* 408.1 (2002): 51-58.
- [30] Korotcenkov, G., et al. "Faceting characterization of tin dioxide nanocrystals deposited by spray pyrolysis from stannic chloride water solution." *Thin solid films* 471.1 (2005): 310-319.