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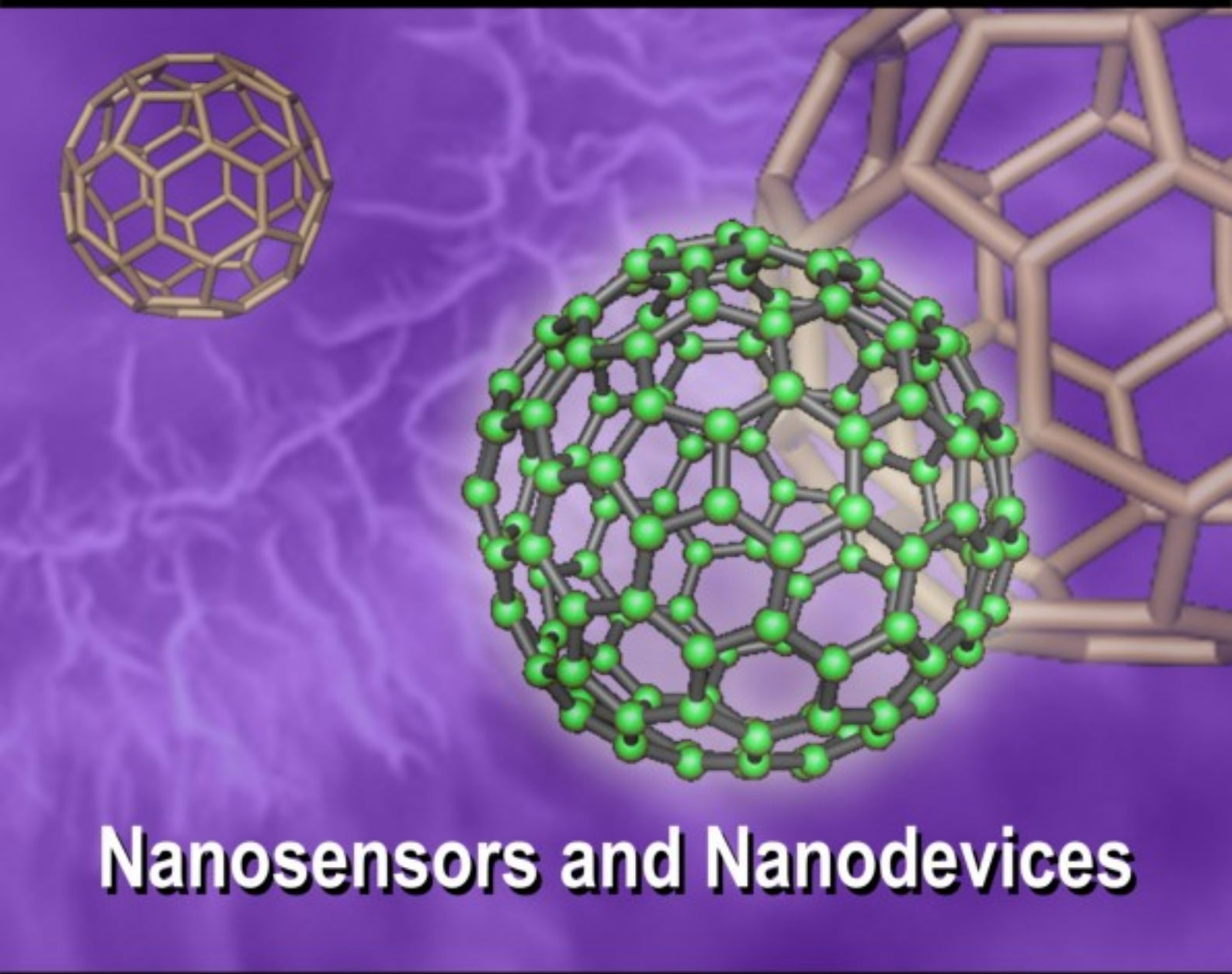

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Gas Sensing Properties of Indium Tin Oxide Nanofibers

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Abstract: Indium Tin Oxide (ITO) nanofibers were fabricated by the electrospinning process. The morphology and crystal structure of ITO nanofibers were studied by SEM, XRD, and TEM respectively. The results showed that polycrystalline ITO nanofibers with an average diameter of 80 nm were obtained. Sensors based on these nanofibers were fabricated by collecting these nanofibers on the integrated sensor platforms. The ITO nanofiber-based sensors showed very fast and high sensor responses at both room and elevated temperatures for NO_2. The ratios of resistance in NO_2 over that in air were 5 at room temperature and 34 at the optimal working temperature, respectively. The ITO nanofiber-based sensor can be repeatedly used. The details for the fast, enhanced sensor responses and the optimal temperature were discussed. *Copyright © 2009 IFSA.*

Keywords: Gas Sensing, electrospinning, ITO, Nanofiber, Sensor

1. Introduction

Chemical sensing based on 1-D nanostructures has attracted enormous attention because these nanostructures are expected to deliver better performance due to their enhanced surface-to-volume ratio and debye length-to-diameter ratio [1]. Silicon nanowires [2], Carbon nanotubes [3, 4] and metal oxides nanowires [5-7] have shown promising sensing performance according to extensive researches. 1-D nanostructures were prepared by various methods including plasma enhanced chemical vapor deposition (PECVD) [8], metal organic chemical vapor deposition (MOCVD) [9], thermal evaporation [10] and sonochemical and chemical reaction [11], which can be classified into vapor phase approaches and wet solution routes. However, simple and effective methods which can integrate with microfabrication for the reliable and controllable production of 1-D nanostructures for sensor applications are still needed. The electrospinning process is a sample way for the fabrication of

1-D nanostructures which have been used for the fabrication of various nanofibers including polymer, inorganic and composites [12-14].

ITO thin films have been extensively used as transparent conducting electrodes in solar cells [15], flat-panel displays (FPD) [16], and organic light emitting diodes (OLEDs) [17] because they have high electrical conductivity, high optical transparency, and smooth surface morphology [18]. It was also found that ITO thin films could also be used for gas sensors to detect methanol, H_2, and NO_2 [19-21]. These sensors showed a very high sensor at relatively high temperatures of 300 ˚C. In contrast, ITO nanolayer-based sensors showed very good performance at low temperature because of the small grain size (30 nm) of the nanolayers which increased the surface-to-volume ratio and decreased the grain size-to-Debye length ratio [22]. Thus, based on our findings in the characterization of nanofibers, ITO nanofibers are expected to have higher sensitivity at lower temperature because they will have a larger surface-to-volume ratio and a smaller grain size.

There is less literature available in reporting the gas sensing properties of ITO nanofibers with diameter smaller than 100 nm. In this paper, we present the fabrication of ITO nanofibers with diameter smaller than 100 nm by electrospinning process. The morphology, crystal structure and nanostructure of ITO nanofibers were investigated. Sensors based on the electrospun ITO nanofibers were fabricated by collecting ITO nanofibers on the integrated sensor platform. The sensor responses of the ITO nanofiber-based sensor were investigated. The results showed the sensors based on the electrospun ITO nanofibers exhibited very high sensitivity to diluted NO_2.

2. Experimental Details

2.1. Fabrication of ITO Nanofibers

The starting materials including Tin (IV) isopropoxide, Indium (III) isopropoxide, poly (vinyl pyrrolidone) (PVP), ethanol and acetic acid were purchased from Aldrich. Ethanol was used as the solvent for PVP. The purpose of adding PVP is to modify the viscosity of the solution for electrospinning, and make it electrospinnable [23]. In addition to PVP and ethanol, acetic acid was added to stabilize the solution and to control the hydrolysis reactions of the precursor [23]. PVP dissolved in ethanol and acetic acid were added to the mixture of Tin isoproxide and Indium isoproxide. The final mixture was vigorously stirred at room temperature for two hours. The optimized ratio of Sn to In was 17 % as described in ref [24] because ITO has the best crystallinity for the best sensor response at this composition.

ITO nanofibers were fabricated by electrospinning process. The electrospinning set-up consists of a high voltage supplier, a stainless steel needle with a diameter of 200 μm and a collecting plate or substrate as described in ref. [25]. The small needle size was chosen so that a small drop of precursor was maintained at the needle tip by the surface tension of the solution. A high voltage was applied to create an electrically charged jet of the precursor solution. The potential difference between the tip and collecting plate was 10 kV. The negative electrode was connected to the collecting silicon substrate. After electrospinning, the as-spun fibers were annealed at 1 atm with different temperatures in a high temperature oven to obtain the proper crystal structure.

The morphologies of ITO nanofibers were imaged by a field-emission scanning electron microscope (SEM) (LEO 982) operated at accelerating voltages of 5 kV and 2 kV and the diameters of the nanofibers were measured. The X-ray diffraction (XRD) patterns were recorded using the Simens 6000 (Cu Kα radiation) at scanning rate of 0.05º with 2θ ranging from 20º to 70º. The Transmission electron microscope (TEM) (Philips CM20) operated at 200 kV was used to investigate the nanostructures of

the ITO nanofibers. The electric properties of the ITO nanofiber-based sensor were characterized by a Keithley 4200-SCS Semiconductor Characterization System.

2.2. Fabrication and Testing of the Sensor

The basic concept of an ITO nanofiber-based sensor is shown in Fig. 1, which basically consists of ITO nanofibers and electrodes. For the purpose of performance optimization, the integrated sensor platforms were used to collect the ITO nanofibers and fabricate the ITO nanofiber-based sensor. The structure of the sensor platform is shown in Fig. 2. This MSP632 type sensor platform was purchased from DWM & Associates, Inc., which consists of a built-in microheater, platinum temperature sensor, and a pair of interdigitated electrodes. The microheater and the temperature sensor are used to maintain a constant temperature. The interdigitated electrodes (IDEs) are used for the sensor itself for making a resistant type connection as shown in Fig. 1. The as-spun ITO nanofibers deposited on the sensor platform were annealed at 873 K for 2 h.

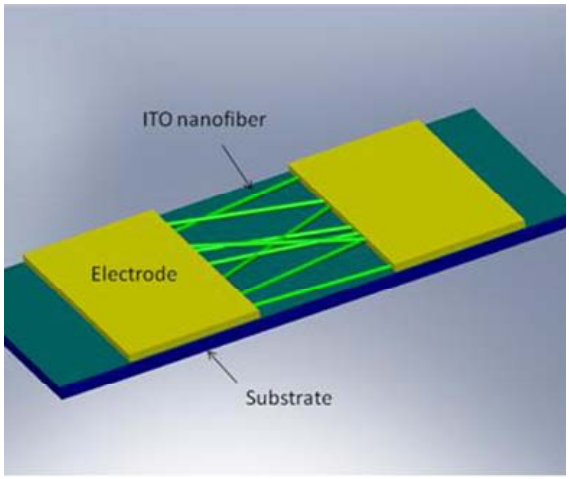

Fig. 1. Schematic an ITO nanofiber-based sensor.

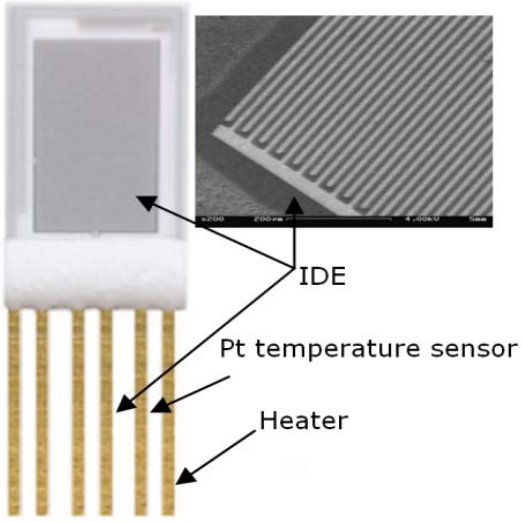

Fig. 2. Structure of the sensor platform (left) and SEM image of the IDE (right).

The diluted NO_2 (100 ppm in dry air) was injected into the testing chamber and resistances of the gas sensors were measured by an Agilent 34401A digital multimeter which was connected to a computer to save the real-time data. Since resistance of the ITO nanofibers in the presence of NO_2 will increase, the sensor response was defined by equation (1) [18]:

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

where R_a and R_g are the resistance of ITO nanofiber based sensor in air and in targeted gases, respectively. The working temperature of the sensors was adjusted through varying the heating voltage and the resistance of the sensors at different temperatures was recorded.

3. Results and Discussion

The morphology of ITO nanofibers obtained by the electrospinning process is shown in Fig. 3. Randomly distributed ITO nanofibers were shown to have been collected on the silicon substrate; these nanofibers were continuous in a very long range (larger than 100 μm) even after the annealing process. No particles were observed, thus, the yield of the fabrication of ITO nanofibers was 100 %. The long nanofiber length would contribute to the good connection of the final sensors. The average diameter of the collected nanofibers was 80 ± 8 nm which was calculated from 100 randomly measured nanofibers. As shown in Fig. 4, an individual nanofiber was shown with uniform cross section and a diameter of 67 nm. The average diameter was much smaller than the reported value in ref. [26], which was 220 nm. Since the precursor of ITO can be rapidly hydrolyzed by the moisture in the air, continuous jets of the ITO precursor were able to be converted into composite nanofibers once they had been ejected from the needle. As the PVP was selectively removed by annealing the sample in air at 500°C, the nanofibers remained as continuous structures which were the finally obtained ITO nanofibers. The average diameter of the annealed nanofibers was smaller than that of the as-spun fibers. This size reduction was attributed to the loss of PVP from the nanofibers and the crystallization of ITO during the annealing process. The average diameter of nanofibers fabricated by the electrospinning process can be tuned by varying the PVP concentration in the precursor [25].

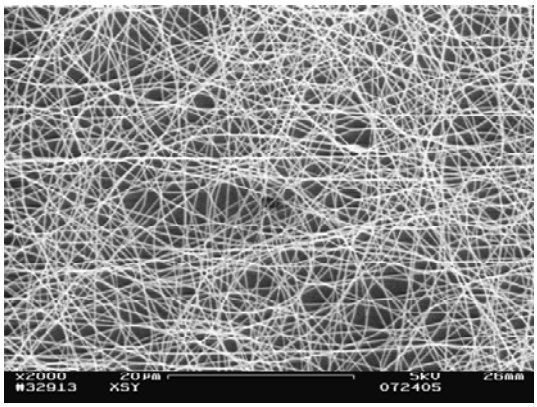

Fig. 3. SEM image of ITO nanofibers.

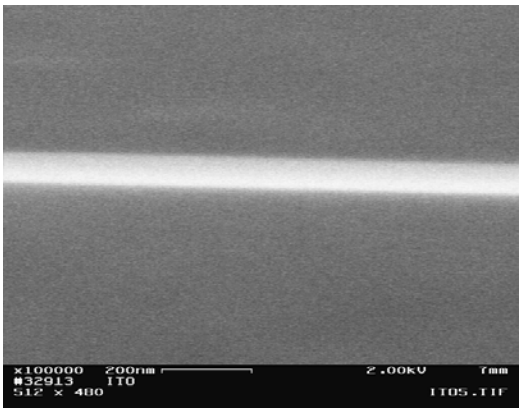

Fig. 4. SEM image of a single PZT nanofiber.

Fig. 5 shows the X-ray diffraction (XRD) patterns of the annealed ITO nanofibers. The peaks were indexed as (211), (222), (400), (440) and (622) crystal faces of ITO which confirmed that the annealed ITO nanofibers were polycrystalline. Fig. 5 also shows that the diffraction peak at $2\theta=30.43^{\circ}$, corresponding to the (222) PZT plane, was obviously stronger than other peaks. This indicated a strong preferred crystal orientation along the [222] direction. The added PVP played an important role in the preferential nucleation and growth of ITO nanofibers. By increasing the annealing temperature, the peak intensity of ITO nanofibers in the XRD pattern was increased because the crystallinity was improved.

The TEM image of an ITO nanofiber is shown in Fig. 6. The diameter of the selected ITO nanofiber was about 100 nm. The TEM image also revealed that the grain sizes of the ITO nanofibers ranged from 17 nm to 24 nm which are smaller than that of the ITO nanolayers as described in ref. [22]. And there were some voids in the nanofiber. These voids might contribute to the sensor response of the ITO nanofibers because they increased the surface-to-volume ratio. The Selected Area Diffraction (SAD) pattern shown in Fig. 7 confirmed the polycrystalline characteristic of the annealed ITO nanofibers as shown in XRD patterns.

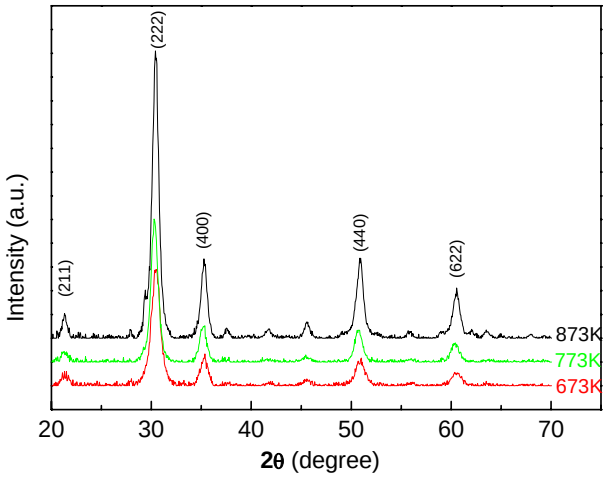

Fig. 5. XRD patterns of ITO nanofibers annealed at different temperatures.

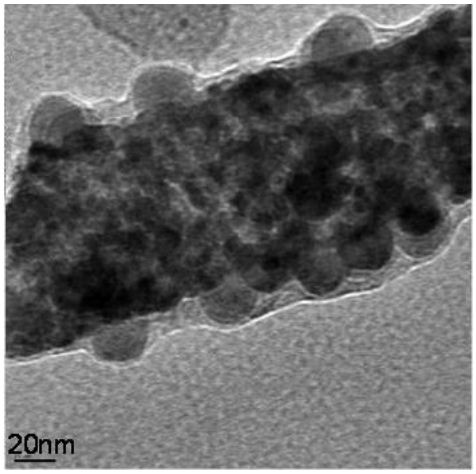

Fig. 6. TEM image of an ITO nanofiber.

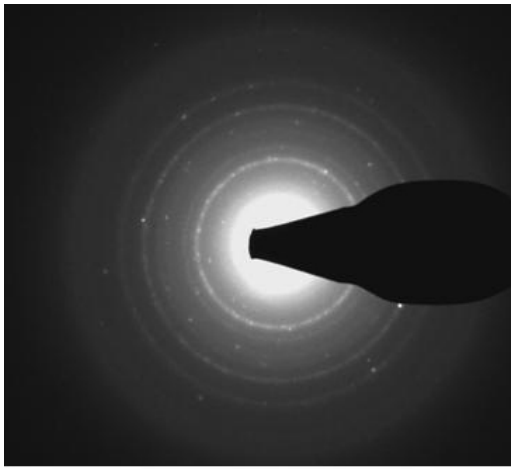

Fig. 7. SAD pattern of an ITO nanofiber.

The SEM image of ITO nanofiber-based sensor is shown in Fig. 8. The distributions of ITO nanofibers on the IDEs were observable. The ITO nanofibers bridged the IDEs and formed resistor-like structures as shown in Fig. 1.

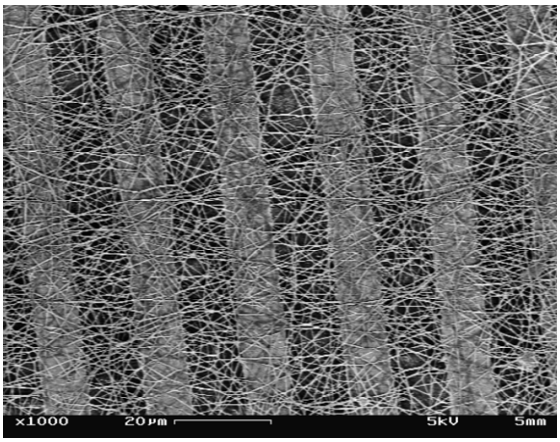

Fig. 8. SEM image the ITO nanofiber-based sensor (the ITO nanofibers on the IDEs).

A typical I-V curve of the nanofibers on the integrated sensor platform is shown in Fig. 9. This I-V curve showed a linear relationship which indicated that the ITO nanofibers and IDEs had a very good ohmic contact and no further metal electrode deposition was needed to integrate the sensor. The resistance of the sensor was 3.7 kΩ.

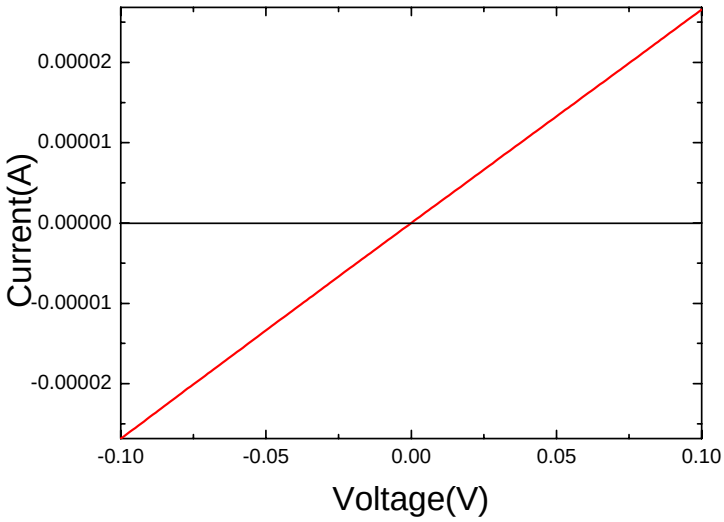

Fig. 9. The I-V curve of the ITO nanofibers on the sensor platform.

Fig. 10 shows a representative sensor response the ITO nanofiber-based sensor worked at room temperature. The resistance increased sharply when NO_2 was filled into the testing chamber. The sensor response of ITO nanfiber-based sensor at room temperature was about 5, which was very high and had not been reported by other group yet. It took quite long for the sensor to return to the original state. The reason might be that the desorption process was slower when temperature was low. When the temperature of the sensor was increased to a high temperature as 250°C and then lowered to room temperature, the resistance was reduced to the original value very quickly as shown in Fig. 11. This suggests that the resistance increase is reversible and ITO nanofiber-based sensor can be repeatedly used.

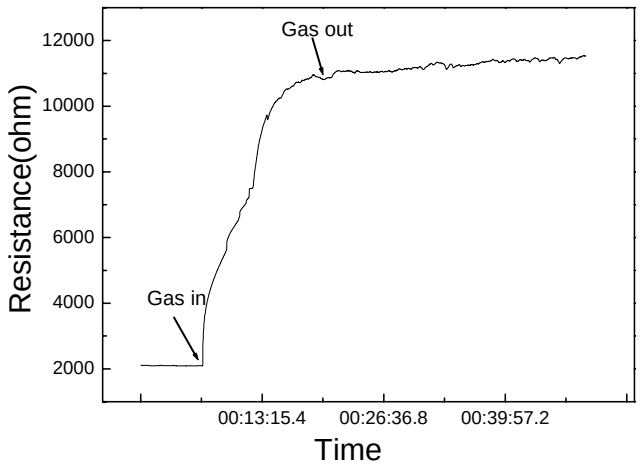

Fig. 10. Sensor response of an ITO nanofiber-based sensor work at room temperature.

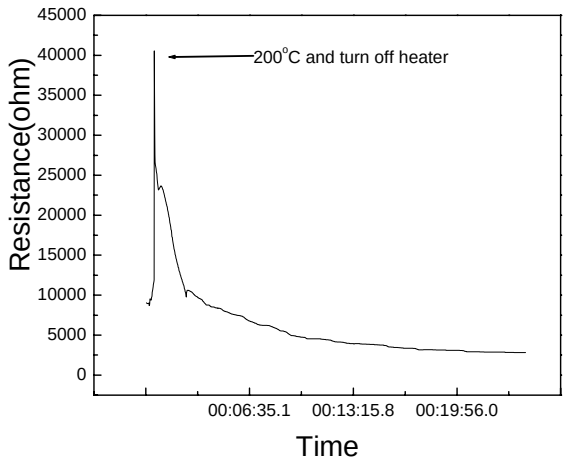

Fig. 11. The recovery process of the ITO nanofiber-based sensor.

Fig. 12 shows the sensor response of the ITO nanofiber-based sensor at 300 °C. The sensor showed a very quick response to NO_2 at elevated temperature and the sensor again returned to the original state quickly when the gas was purged out. The sensor response at this temperature was 34, which was much higher than that of ITO thin films, which was 5 as reported by other researchers [18]. The optimal temperature for the detection NO_2 under 1 atmosphere is about 300 °C as shown in Fig. 13. The fast response could be attributed to the full exposure of the ITO nanofiber surface area to the chemical environment which was full of NO_2 molecules. The reason for the better performance might be resulted from the higher surface-to-volume ratio. ITO nanofibers have very large surface-to-volume ratio which means a significant fraction of the atoms of ITO are surface atoms that can participate in surface reactions. This feature would contribute to the resistance change of the ITO nanofibers, thus enhance the sensor response and lower the working temperature. Another reason was related to the nature of the ITO surface which was prone to react with NO_2 [27]. Semiconductor gas sensors are based on the conductivity changes of the semiconductor materials upon interaction with the target gas molecules [28]. When the NO_2 molecules were absorbed on the surface of the ITO nanofibers, electron transfer occurs between ITO and NO_2. NO_2 molecules reacted with ITO at a lower temperature and were absorbed into the adsorption sites. When the temperature was increased, the molecules were easier to react and be absorbed on the adsorption sties. However, desorption process existed at the same time. When the temperature was too high, the desorption process would dominate which lowered the net absorption of NO_2. Thus, there was an optimum working temperature for ITO nanofiber based sensor. A systematic investigation is underway. Besides the sensitivity, other parameters such as selectivity, response time and stability, are also very important. The testing for these parameters is in progress.

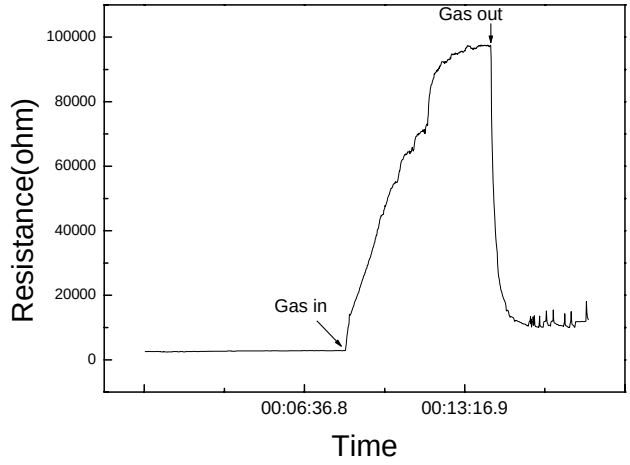

Fig. 12. Sensor response of an ITO nanofiber-based sensor work at 300 °C.

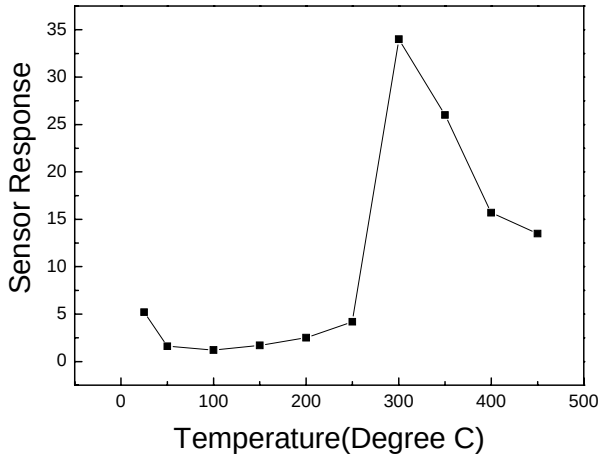

Fig. 13. The curve of sensor response *vs* temperature.

4. Conclusions

In conclusion, we have shown that ITO nanofibers fabricated by electrospinning process exhibits pronounced gas sensing properties for NO_2. The main advantage of these ITO nanofibers, besides their small diameters (lower than 90nm), is that they can operate at room temperature with sensor response as high as 5 or at the optimal temperature with sensor response of up to 34. The fast response should be caused by that the whole surface of the ITO nanofiber surface area is easy to be fully exposed to the NO_2 and the enhanced sensor response can be attributed to the enhanced surface-to-volume ratio achieved by the decreased diameter and grain size. The active surface of ITO should also be related. Thus the ITO nanofibers are promising for advanced miniaturized gas sensors.

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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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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
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