# 整合氧化鎢感測層與加熱裝置之微型苯氣體感測器
# A MEMS-based Benzene Gas Sensor with $WO_3$ Sensing Layer and Integrated Micro-hotplate

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*摘要*

本文乃製作一以微機電技術為基礎之苯氣體感測器，其中以石英材料作為基材，並以白金製作指叉電極與微加熱器，且透過沉積氧化鎢薄膜做為氣體感測層。當環境空氣中帶有苯氣體時，會於加熱之氧化鎢感測層表面產生氧化反應，進而改變氧化鎢薄膜之導電特性，故可經白金指叉電極量測其阻值變化量。而苯氣體濃度可經所量測之阻值推算而得。本文之氧化鎢薄膜可由已最佳化之濺鍍參數進行沉積而得，並且當感測器之工作溫度於 300°C 時可獲得最佳之感測特性。由實驗數據顯示，本文之感測器不僅具有高靈敏度之特性 (9.86 % $ppm^{-1}$)，更擁有快速的反應時間 (40 s) 與回復時間 (240 s)。

*關鍵詞*：苯，氣體感測器，微加熱器，微機電系統，氧化鎢薄膜

*Abstract*

This study develops a MEMS-based benzene gas sensor consisting of a quartz substrate, a thin-film $WO_3$ sensing layer, an integrated Pt micro-hotplate, and Pt interdigitated electrodes (IDEs). When benzene is present in the atmosphere, oxidation occurs on the heated $WO_3$ sensing layer. This causes a change in the electrical conductivity of the $WO_3$ film, and hence changes the resistance between the IDEs. The benzene concentration is then computed from the change in the measured resistance. A specific orientation of the $WO_3$ layer is obtained by optimizing the sputtering process parameters. It is found that the better sensitivity of the gas sensor is at a working temperature of 300°C. At the working temperature, the experimental results show that the sensor has a high degree of sensitivity (9.86 % $ppm^{-1}$), a rapid response time (40 s), and a quick recovery time (240 s).

*Keywords*: benzene, gas sensor, micro-hotplate, MEMS, $WO_3$ thin film

## I. INTRODUCTION

The presence of volatile organic compounds (VOCs) in indoor environments can cause irritation of the ears, nose and throat and may produce an unpleasant odor [1]. Of these VOCs, benzene ($C_6H_6$) arouses particular concern due to its toxicity and carcinogenic properties. Benzene is carcinogenic via all routes of exposure and is known to be a major cause of leukemia and lymphomas [2].

VOCs are generally detected using some form of conventional gas chromatography technique combined with mass spectrometry (MS). However, such methods are unable to provide benzene exposure information on a real-time basis. As a result, a number of researchers have developed optical sensors for gas quantification applications [3-6]. However, the optical arrangements of these sensors tend to be somewhat bulky and elaborate. Over the past decade, MEMS technologies and micromachining techniques have facilitated the miniaturization of all manner of devices, including gas sensors. The advances made in MEMS technology now enable the acquisition of sensing information at a micro-scale level [7-12].

Many researchers have demonstrated the suitability of thin or thick $WO_3$ films as sensing layers for gas monitoring applications [13-18]. Wang *et al.* [13] fabricated monolithic thin-film metal-oxide gas sensor arrays to detect the presence of VOCs. In their study, microfabrication techniques and a reactive radio frequency (RF) sputtering process were used to deposit $SnO_2$, ZnO and $WO_3$ sensing layers on silicon substrates to monitor the concentrations

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Manuscript received 13 November 2007; revised 13 August 2008; accepted 30 September 2008

of benzene, toluene and methanol, respectively, in air. Tomchenko *et al.* [14, 15] fabricated $WO_3$ thick-film gas sensors using a screen-printing technique. The results showed that a sensing layer thickness of 15 μm optimized the sensing performance over a concentration range of 2 to 300 ppm NO gas at a working temperature of 300°C. Penza *et al.* [16] also presented a $NO_x$ gas sensor featuring a $WO_3$ sputtered thin film. In this case, it was shown that the sensitivity of the device was optimized by specifying the thickness of the $WO_3$ sensing layer as 4800 Å and the working temperature as 250°C [17]. Lee *et al.* [18] presented a $WO_3$-based nanocrystalline thick film gas sensor. The results showed that the nano-scale grain size of the $WO_3$ sensing layer enhanced the sensitivity of the device, resulting in a good sensitivity to low level $NO_x$ concentrations (0.5-30 ppm) at a working temperature of 350°C.

$WO_3$ possesses good sensing characteristics for the detection of $NH_3$ and $O_3$ in air [19-21]. Llobet *et al.* [19] used a drop-coating method to fabricate $WO_3$ sensors to monitor $NH_3$ in air. The sensitivity of the device was found to be enhanced at a working temperature of 300°C. $O_3$ gas sensors have been successfully developed by printing $WO_3$ porous layers directly onto impermeable substrates [20] and by using a RF reactive magnetron sputtering technique [21].

In the previous studies, $WO_3$ sensing layer was well developed to detect $NO_x$, $NH_3$ and $O_3$ in air. Its application to function as a VOCs (e.g. benzene) gas sensor was less proposed. This study employs a straightforward MEMS-based fabrication process to realize a benzene sensor featuring a quartz substrate, a sputtered $WO_3$ layer with a micron-scale grain size, an integrated Pt micro-hotplate and Pt interdigitated electrodes (IDEs). It is found that the better sensitivity of the gas sensor is at a working temperature of 300°C. At the working temperature, the experimental results show that the sensor has a high degree of sensitivity (9.86 % $ppm^{-1}$), a rapid response time (40 s), and a quick recovery time (240 s).

## II. SENSOR DESIGN

### 1. Micro-hotplate

The sensor developed in this study operates on the principle that changes in the coverage of the adsorbed or chemisorbed gas species on the sensing film cause a detectable change in the electrical conductance of the film. Gas sensing devices are typically designed to operate at elevated temperatures in order to activate the reactions which produce the sensor response and to reduce humidity effects [22]. However, a drawback of such devices is that the observed response may actually be the result of the presence of more than one gas in the atmosphere. Therefore, to enhance the "selectivity" of a device, its operating temperature must be optimized in order to reduce the effects of competing reactions. In the present study, a Pt micro-hotplate is fabricated on the sensing layer [23]. When a voltage is applied to this hotplate, its temperature increases, generating a simultaneous heating effect in the sensing layer immediately below it. The operating temperature for the sensor is determined by varying the temperature of the hotplate, i.e. by varying the applied voltage, and comparing the detection sensitivities at different temperatures.

### 2. Design

As shown in Figure 1, the benzene sensor developed in this study comprises a quartz substrate, a $WO_3$ sensing layer, a Pt micro-hotplate, and Pt IDEs. To avoid substrate's broken failure in the heating process, the quartz material was chosen due to its low thermal expansion coefficient (5.5 X $10^{-7}$ 1/°C) in comparison with those of glass (8.8 X $10^{-6}$ 1/°C) or silicon (2.6 X $10^{-6}$ 1/°C). The micro-hotplate provides an instantaneous and precise temperature control capability, while the IDEs facilitate the direct electrical measurement of the change in conductivity of the sensing layer induced by the presence of benzene in the atmosphere. The grain size of the sputtered $WO_3$ sensing layer is very small, and therefore both the sensitivity and the response time of the device are enhanced due to the increased contact area between the catalyst grains and the sensed gas.

## III. FABRICATION

### 1. Thin film deposition

The $WO_3$ films were prepared using an RF magnetron sputtering system with a W target of 99.99% purity [24-26]. The oxide layer was sputtered on a quartz substrate located at a distance of 11.4 cm from the W target. Sputtering was performed under a gas pressure of 0.01 torr with the target maintained at a constant RF power of 200 W. The reactive sputtering gas was a mixture of argon (50%) and pure oxygen (50%). Prior to deposition, the chamber was pumped to a background pressure of $10^{-6}$ torr for 1 h and a pre-sputtering process was performed for 10 min to remove any traces of contamination from the target

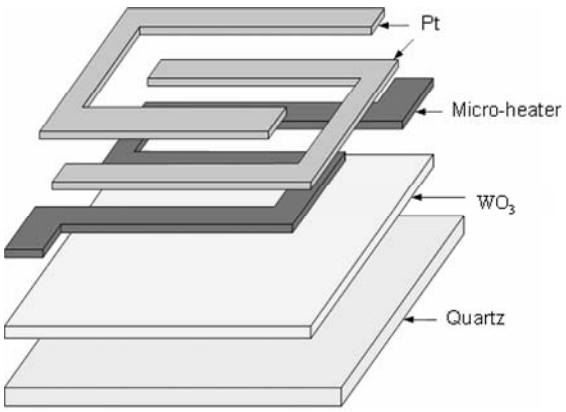


Fig. 1 Schematic illustration of benzene sensor with integrated micro-hotplate and IDEs

surface. Subsequently, RF sputtering was performed for 10 h, resulting in a $WO_3$ film with a thickness of approximately 4.4 μm.

## 2. Microfabrication

Figure 2 presents a schematic illustration of the fabrication process used to realize the current benzene sensor. Following the deposition of the 4.4-μm thick $WO_3$ sensing layer on the quartz substrate, a thin layer of Cr (0.05 μm) was deposited to serve as an adhesion layer for a Pt layer (0.2μm) deposited using an electron-beam evaporation process. A standard lift-off technique was then employed to pattern the Pt micro-hotplate and IDEs. The resistance of the hotplate was designed to be 30 Ω. Following the lift-off patterning process, the sensor was annealed in dry air. In the annealing process, the sensor was heated from 25°C to 400°C over a period of 2 h, then maintained at a temperature of 400°C for 24 h, and finally cooled back down to 25°C over 2h.

Figure 3 presents an SEM image of the cross-section of the completed gas sensor. Figure 4(a) shows an SEM photograph of the as-deposited $WO_3$ thin film. From inspection, the grain size is found to be approximately 10 μm. Figure 4(b) presents the surface morphology of the annealed $WO_3$ thin film. It can be seen that the annealing process causes the grain size to increase and the gap between neighboring grains to reduce. Hence, it is apparent that annealing fails to reduce the grain size and therefore does not enhance the sensing performance of the sensor.

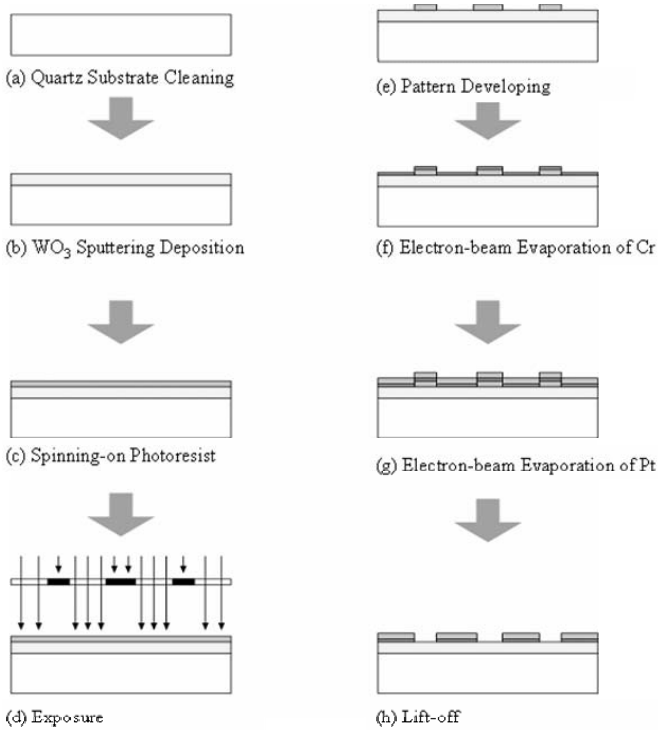


Fig. 2 Overview of fabrication process for $WO_3$ thin-film-based benzene sensor

Finally, the SEM image in Figure 5 reveals the porous nature of the Pt micro-hotplate / IDE surface. This characteristic has a favorable effect in enhancing the permeability of the sensed gas through the metal layer to the underlying $WO_3$ sensing film.

## IV. RESULTS AND DISCUSSION

The diffraction pattern of the $WO_3$ sensing layer was observed using an XRD measurement system (XRD-600 LabX, Shimadzu, Japan). The heating performance of the micro-hotplate was investigated using an IR thermometer (PT-3LF, OPTEX, Japan). The sensing performance of the device was characterized in a test chamber by using an LCR meter (4230 LCR, Wayne Kerr Electronics, Taiwan) to record the signal response generated by changes in the benzene concentration over the range 0 to 1400 ppm.

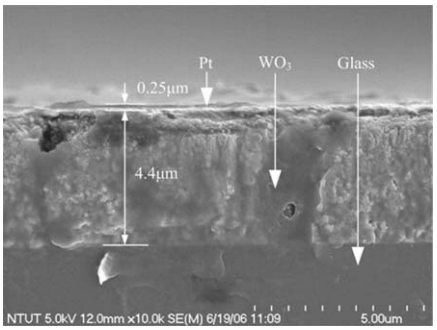


Fig. 3 SEM image showing cross-section of benzene sensor

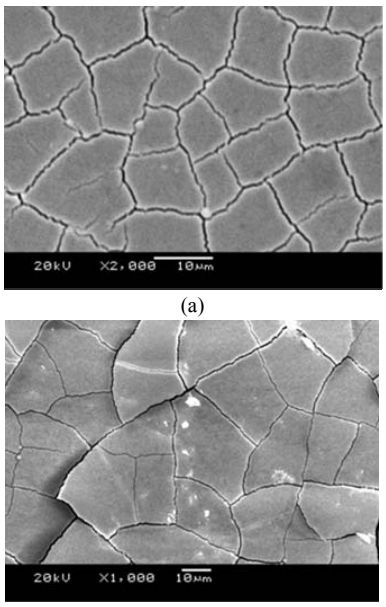


Fig. 4 SEM image showing micrometer grain size of sputtered $WO_3$ thin films: (a) as-sputtered condition, and (b) annealed condition

Figure 6 shows the diffraction pattern of a $WO_3$ thin-film sample deposited at a sputtering temperature of 25°C. In general, when a thin film is to be used as a sensing layer, it is desirable that the film has a non-random orientation. In Figure 6, it is apparent that the specified sputtering annealing conditions result in a $WO_3$ film with good crystallinity and a pronounced (002) preferred orientation.

Figure 7 presents the variation of the micro-hotplate temperature with the applied power. It can be seen that the temperature increases linearly with increasing power at a rate of approximately 54°C/W.

Figure 8 shows the variation in the resistance response of the gas sensor as a function of the working temperature for benzene concentrations ranging from 0 to 1400 ppm. An approximately linear dependency is observed between the resistance and the benzene concentration at each working temperature. The measurement accuracies are statistically evaluated by $R^2$ values, which are 0.92, 0.98 and 0.81 at 250°C, 300°C and 350°C, respectively. It is found, a better accuracy of measurement is at the working temperature of 300°C.

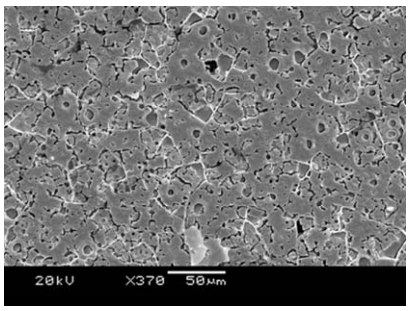


Fig. 5 SEM image showing porous surface of Pt thin film

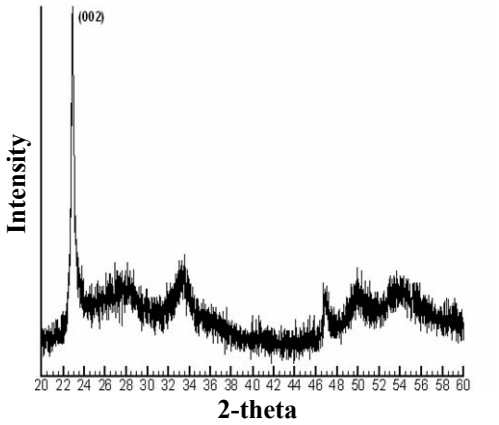


Fig. 6 XRD diffraction pattern of $WO_3$ film deposited at room temperature. (Note: sputtering conditions as follows: Target, 99.99% $WO_3$; RF power of target, 200 W; argon flow rate, 15 sccm; oxygen flow rate, 15 sccm; working pressure, 0.015 torr.)

The sensitivity of the sensor is assessed using the following sensitivity factor:

$$S = \frac{R_a}{R_g} \quad (1)$$

where $R_g$ is the sensor resistance in the presence of benzene and $R_a$ is the sensor resistance in air [27]. Figure 9 plots the variation of the sensitivity factor with the benzene concentration as a function of the working temperature. The slopes of the curves represent the sensitivity of the device and are found to be 0.024% $ppm^{-1}$ at 250°C, 0.041% $ppm^{-1}$ at 300°C and 0.013% $ppm^{-1}$ at 350°C, respectively. A better sensitivity can also be observed at the working temperature of 300°C. The reaction paths of $WO_3$ were proposed in Ref [28].

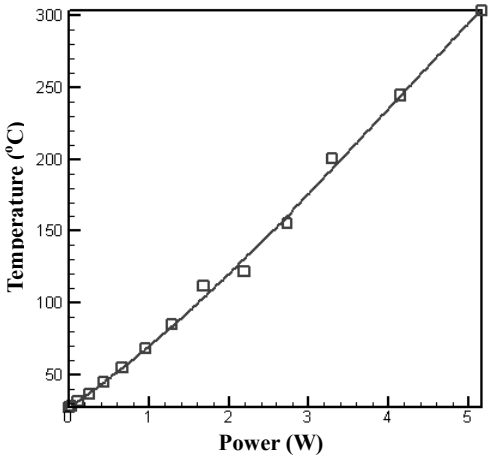


Fig. 7 Variation of micro-hotplate temperature as function of applied power

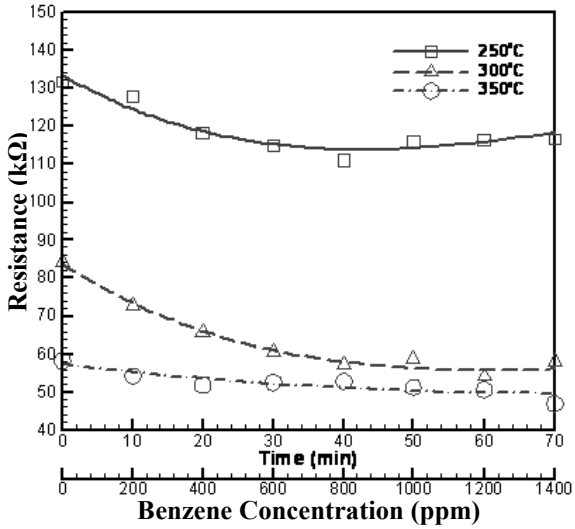


Fig. 8 Sensitivity of benzene sensor as function of working temperature. (Time is measured as the benzene concentration varies.)

In order to determine the benzene concentration sensitivity of the gas sensor, the resistance was measured as the benzene was increased from 0 ppm to 7 ppm in steps of 1 ppm at constant temperature of 300°C. The corresponding results are shown in figure 10. The benzene concentration sensitivity is 9.86% $ppm^{-1}$ at 300°C in the current study.

In conventional gas measurement devices, the time required for benzene concentration measurement can vary from hours to days. However, a requirement exists for sensors with a real-time gas detection and measurement capability. Figures 11(a)~11(c) present the time response of the benzene gas sensor at various working temperatures as the benzene concentration is increased from 0 to 200 ppm. From inspection, the average time constants of the gas sensor are found to be 70 s, 40 s and 20s at working temperatures of 250°C, 300°C and 350°C, respectively.

Figure 12 presents the repeatability results obtained by repeatedly increasing the concentration from 0 to 200 ppm, maintaining this concentration for a period, and then reducing to 0. The results indicate that the benzene gas sensor has a recovery time of 120 s, 240 s and 90 s at working temperatures of 250°C, 300°C and 350°C, respectively. The recovery time reduces as the sensing layer temperature increases to be 350°C due to the offered thermal and kinetic energy for returning the chemical reactions within the sensing layer at the temperature for recovery characteristics.

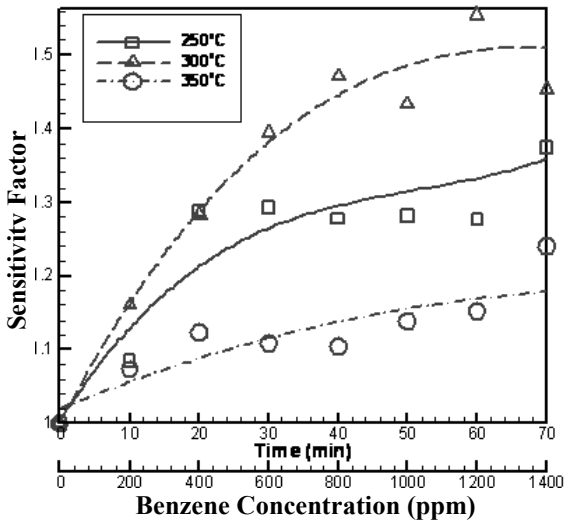


Fig. 9 Variation of sensitivity factor of benzene sensor with benzene concentration as function of working temperature. (Time is measured as the benzene concentration varies.)

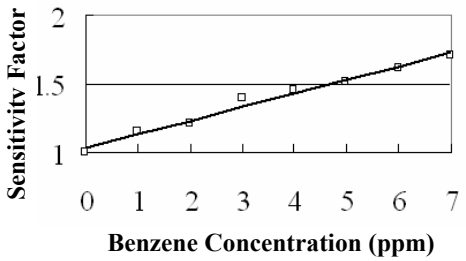


Fig. 10 Sensitivity of benzene sensor at a working temperature of 300°C

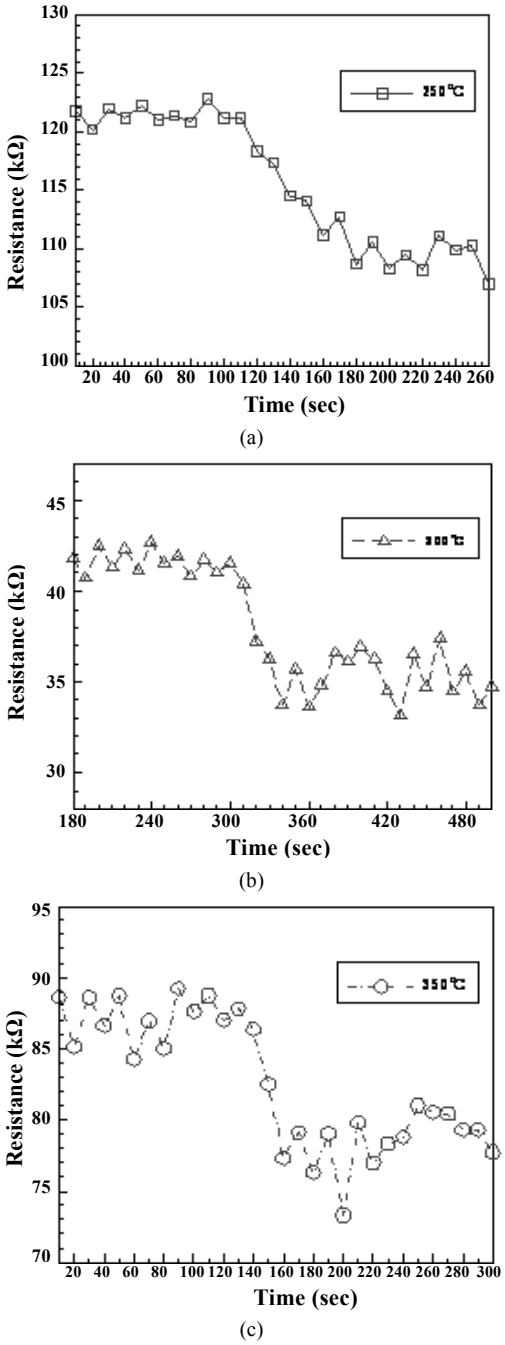


Fig. 11 Time response of benzene sensor when benzene concentration is increased from 0 ppm to 200 pm at working temperatures of: (a) 250°C, (b) 300°C, and (c) 350°C

In the current study, the effects of IDE size, $WO_3$ layer thickness, $WO_3$ orientation and environmental humidity on the sensing performance were not proposed and they will be investigated in the study of the future. Stability and selectivity tests are also required to improve the characteristics of the $WO_3$ sensors in the next study.

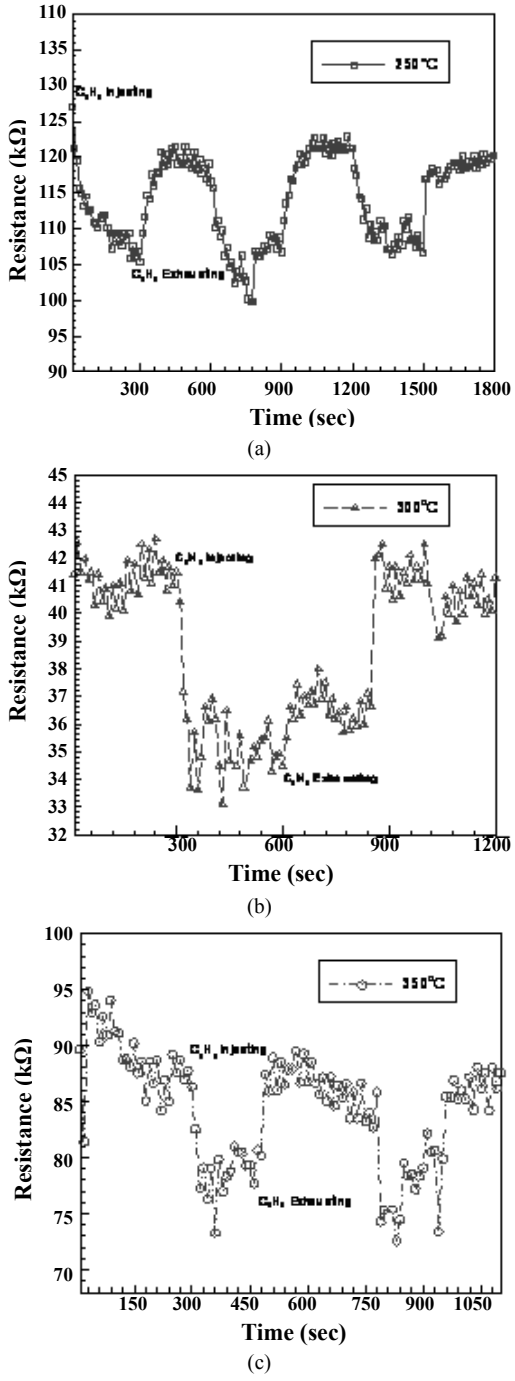


Fig. 12 Repeatability of benzene sensor when benzene concentration is increased from 0 ppm to 200 pm at working temperatures of: (a) 250°C, (b) 300°C, and (c) 350°C.

## V. CONCLUSIONS

This study has demonstrated a novel MEMS-based benzene gas sensor featuring a thin $WO_3$ sensing layer. The $WO_3$ film is deposited on a quartz substrate and a Pt micro-hotplate is then deposited directly on the sensing layer. Finally, Pt IDEs are deposited on the sensing layer to measure the change in conductivity caused by benzene oxidation on the $WO_3$ surface. The integrated micro-hotplate simplifies the detection setup and provides the advantages of good temperature control and low power consumption. The proposed sensor has a high degree of sensitivity, a rapid response time, and a quick recovery time. The sensor is suitable not only for industrial process monitoring, but also for the detection of benzene concentrations in indoor environments in order to safeguard human health.

## ACKNOWLEDGEMENTS

The authors would like to thank the financial support provided by the National Science Council in Taiwan (NSC 97-2221-E-020-038, NSC 96-2218-E-006-004 and NSC 97-2218-E-006-012).

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