

Influence of water vapor on CO detection using a resonant microcantilever functionalized by Al-doped ZnO nanorods

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Abstract

Al doping in zinc oxide nanorods showed a significant increase in the sensitivity of microcantilever CO sensor. In ambient condition, the gas detection using metal oxide was influenced by humidity. In this work, effect of water vapor on CO detection and sensor sensitivity was investigated at varied humidity condition. It was found that the water vapor interaction with the sensitive layer makes CO adsorption easier and thus the sensor sensitivity increased as the humidity increased.

1. Introduction

Microcantilever (MC) is a promising tool for gas sensor due to rapid response, high sensitivity and operation at room temperature. In sensor application, a sensitive layer is coated to effectively detect a target molecule. To detect carbon monoxide (CO) gas, several materials such as polymer [1] and metal complex [2] have been used as sensitive layer. However, zinc oxide nanorods (ZNRs) are also very promising due to their high surface area and subsurface oxygen vacancies to detect the gas. ZNRs have been used as a sensitive layer of the MC to detect water vapor [3] and volatile organic compounds (VOCs) [4]. Many efforts have been done to improve ZNRs-based gas sensor sensitivity. Previously, we reported the effect of Al doping in ZNRs on CO detection using a resonant MC. A significant increase in the sensitivity up to femtogram level was achieved [5].

In ambient condition, the gas detection using metal oxide is influenced by the presence of humidity [6]. Generally, the surface is fully covered by molecularly adsorbed water which should be considered for investigating the characteristic of sensor response [5]. Moreover, the detail of CO sensing mechanism using metal oxide-based MC sensor at room temperature is not reported.

In the present work, we prepared Al/ZNRs on the MC surface as sensitive layer for CO detection. Effect of water vapor on the gas adsorption and sensor sensitivity is investigated by the resonance frequency shift of the MC at varied humidity conditions.

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2. Methods

Preparation of Al/ZNRs sensitive layer

First, a 30-nm seed layer of ZnO was deposited on the MC substrate by the RF magnetron sputtering. Second, ZNRs were grown on the ZnO seeded substrate. A solution of 0.04 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.04 M $\text{C}_6\text{H}_{12}\text{N}_4$ were prepared in deionized water. The substrate was then dipped in the mixed solution for 60 °C for 2 hours. Next, the sample was dried at 90 °C for 30 minutes in an oven. Al was deposited on the ZNR-coated microcantilever (AZNMC) by RF sputtering with a RF power of 100 W and an Ar flow rate of 18 sccm for 105 s.

Sensor system and gas sensing

A piezoresistive microcantilever (NPX1CTP003, SII nanotechnology, Seiko Instrument Inc., Japan) with a typical piezoresistor resistance of 630 Ω was used for the study. The MC with Al-doped ZNRs (AZNMC) was placed in a stainless-steel chamber for the measurement. An uncoated MC was included as a reference. Next, CO gas was flowed into the chamber with the flow rate of 10–100 ml/min. The experiments were conducted at vacuum and varied relative humidity (RH) conditions, i.e. at 46%, 51%, 55%, and 58% RH.

The resonance frequency of AZNMC during the measurement was recorded by a drive-frequency sweeper system with a vibration-amplitude detector controlled by a computer. Here, the resonance frequency was detected as the frequency at the peak amplitude. Response due to CO gas was detected by observing the shift in the resonance vibration frequency.

3. Result and discussion

Characterization of Al/ZNRs sensitive layer

The morphology of the ZNRs layer was monitored using FE-SEM whereas the atom elements were investigated using EDS. The ZNRs layer on the MC surface formed a nanorod structure (Fig. 1). The average diameter of the high-density nanorods was approximately 100 nm. EDS spectra showed Al mass of 1.76 % on the ZNRs layer.

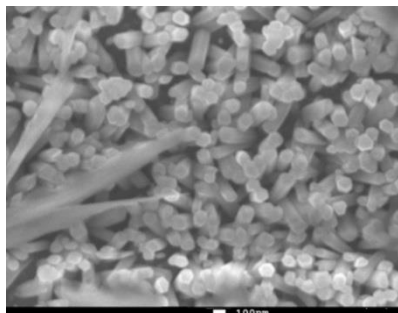


Fig. 1 FE-SEM images of ZNRs on microcantilever surface.

Effect of water vapor on CO detection

The resonance frequency of AZNMC due to CO insertion was observed at varied RH. It was found that the frequency shift remarkably increased with increasing the inserted CO flow rate, as shown in Fig. 2. It was also found that the resonance frequency of uncoated MC was not changed during the measurement. For 46% and 51% RH, the change in resonance frequency of AZNMC at 60 and 80 ml/min CO was not obvious, however, it clearly appeared on for 55% and 58% RH. Mostly, the frequency shift of AZNMC rose up at increased water vapor content.

The sensitivity was calculated by using the equation, $dm/df = 2 \times m/f$ for AZNMC. Here, m is the mass and f is the initial resonance frequency of MC, dm and df are the mass, and frequency change, respectively. The calculated sensitivity for CO detection at 46%, 51%, 55%, and 58% RH was 7.38, 7.79, 7.74 and 7.82 fg/Hz, respectively. The sensitivity of AZNMC increased with the increase of humidity and such result indicated that the water vapor influenced the sensor sensitivity in CO detection.

The effect of water vapor on CO adsorption can be explained as follows. At room temperature, water vapor formed the dissociated hydroxyl (OH^-) and proton (H^+) ions on AZNMC surface [6,7]. At higher humidity levels, physisorption of water molecules increased the H^+ concentrations on the surface, as a result, more number of H^+ ions exist on the surface and the adsorbed H^+ makes the surface energy less [6]. As the Al/ZNRs surface energy decreases, it becomes capable to make chemical bond with CO. As a result, adsorption of CO molecules by the active sites of the Al/ZNRs surface becomes easier. Therefore, for the more water molecules (i.e., more H^+) on the surface, the more Al/ZNRs will be able to adsorb more CO molecules and increase the sensor sensitivity.

CO detection on vacuum condition was conducted to investigate the gas adsorption on zero RH, as shown in Fig 3. Any significant change in the resonance frequency of AZNMC for 100 ml/min CO could not be observed. Prob-

bly, unavailability of water vapor in the vacuum chamber made the surface energy high and no chemical bond of CO can be formed.

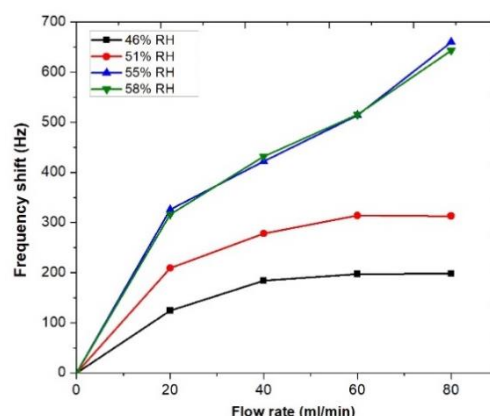


Fig. 2 Frequency shift of the AZNMC due to 20-80 ml/min CO in varied RH.

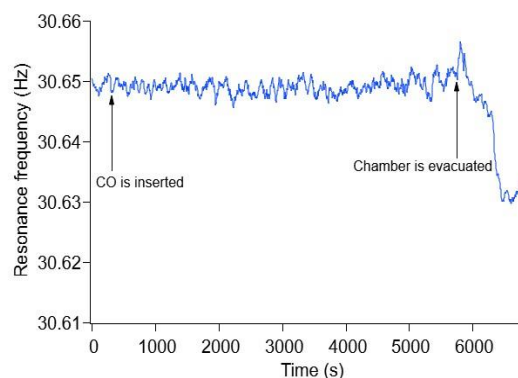


Fig. 3 Response of AZNMC on CO detection in vacuum

4. Conclusions

Al-doped ZnO nanorods was coated on the MC surface as sensitive layer and CO detection was investigated under vacuum and at varied RH conditions. It was found that the water vapor interaction with the sensitive layer reduces the surface energy making CO adsorption easier and thus the sensor sensitivity increased as the humidity increased.

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