Highly sensitive gas sensors on low-cost nanostructured polymer substrates

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SnO$_2$ thin-film gas sensors have been successfully fabricated on nanospiked polyurethane polymer surfaces, which are replicated by a low-cost soft nanolithography method from silicon nanospike structures formed with femtosecond laser Irradiations. Measurements revealed significant response to carbon monoxide (CO) gas at room temperature, which is considerably different from the sensors of SnO$_2$ thin films coated on smooth surfaces that show no response to CO gas at room temperature. The high area/volume ratio and sharp structures of the nanospikes enhance the sensitivity of SnO$_2$ at room temperature. This will greatly decrease the electrical power consumption of the gas sensor and the cost for calibrations, and has great potential for application in other sensing systems.

Keywords: thin-film sensor; tin oxide; carbon monoxide gas; nanospike; soft nanolithography

1. Introduction

Conventional semiconductor oxide gas sensors [1–3] contain a thin surface layer of a semiconducting oxide such as tin(IV) oxide, SnO$_2$, and zinc oxide, ZnO. The presence of minute amounts of the gas of interest is detected from the change in the electrical resistance of this layer. Gas recognition requires adsorption or reaction of gas molecules with the oxide surface, whereas the transduction of the adsorption into a resistance change is controlled by the microstructure of the semiconductor. Establishing sensor selectivity for specific gases is difficult and challenging. Doping the semiconductor with metals such as Pd and Ag increases the sensitivity to some specific gases [4–6]. Previous studies have also indicated that metal oxides coated with gold have important applications for sensor gas selectivity [7,8]. The mechanism of the gas selectivity is not yet well understood. Such conventional gas sensors function at temperatures higher than 150°C [9,10], which not only requires a large amount of energy to maintain the sensors in working mode, but also results in sensor degradation [11].

Attempts have been made to develop gas sensors with high sensitivity and low operating temperatures for commercial applications, based on semiconductors such as SnO$_2$, ZnO, TiO$_2$, MoO$_3$ and Fe$_2$O$_3$ [12–14], but, thus far, making progress toward having semiconductors operating at room temperatures has been difficult. In our previous work [15], we
H. Huo et al. have successfully fabricated a highly sensitive room temperature carbon monoxide (CO) gas sensor on Si nanospiked surfaces [16–18]. However, the fabrication of Si nanospike structures is expensive to develop the sensors for application at low cost. In this work, by combining femtosecond laser nanomanufacturing with soft nanolithography technology [19–22], we have successfully made a SnO2 thin-film gas sensor for detecting CO gas with high sensitivity at room temperature on the polymer nanospike substrates at very low cost. This technology is also applicable to detect other gases.

2. Experimental

In the experiment, the silicon substrates with nanospikes were used as the master mold for the soft nanolithography [22]. As described in previous paper [16], silicon nanospikes were fabricated by irradiating the surface of the silicon substrate in methanol by a femtosecond laser, which has a frequency-doubled output (400 nm wavelength, 100 fs pulse, 1 kHz repetition rate) from an amplified Ti:sapphire laser (Quantronix, USA). The schematic illustration of the soft nanolithography fabrication procedure is shown in Figure 1. First, the as-fabricated silicon wafers with nanospike structures were in sequence rinsed in HF solution to remove the oxide layer, oxygen plasma treated for about 5 min, and coated with 1H,1H,2H,2H-perfluorooctyl-trichlorosilane (PFOTS, Fluka) in a vacuum chamber. So, a silane monolayer with low surface energy formed on the surface of the silicon wafer as an anti-sticking layer. Then, the poly(dimethylsiloxane) (PDMS) mold was made with a spin-coated hard-poly(dimethylsiloxane) (h-PDMS) (~100 μm thick) as the contact layer with the nanospiked surface, and a layer of soft-poly(dimethylsiloxane) (s-PDMS) (~2 mm thick, Sylgard 184 Silicone Elastomer, Dow Corning; Midland, MI) as a back layer. We cured the h-PDMS in an oven at 70°C for about 10 min, and successively poured the s-PDMS and continued curing at 70°C for an additional 3 h. Then the PDMS mold was removed from the silicon substrate. Finally, the nanospike structures were replicated on the surface of the UV-curable polyurethane (PU) polymer by lightly pressing the PDMS mold onto the PU glue (Norland Optical Adhesives, NOA 73; Cranbury, NJ) on a glass substrate and UV-curing for about 5 min.

Figure 1. Schematic illustration of the soft nanolithography fabrication procedure for replicating the nanospike structures.
Figure 2 shows the fabrication procedure of SnO$_2$ gas sensor on the PU nanospikes. First, the PU nanospikes in an area of about 5 mm × 3 mm were replicated using the soft nanolithography method mentioned above. Then, a 150 nm thick Sn layer was thermally evaporated on the PU nanospike substrate with a mask to form a long rectangular pattern with the length of 5 mm and the width of 0.25 mm; after thermal evaporation, the sample was heated on a hot plate at 250°C in air for about 3 h to oxidize the Sn to SnO$_2$ layer [23]. Finally, contact electrodes were fabricated by thermally evaporating about 80 nm thick Au films with another mask. The electrical measurements on the SnO$_2$ gas sensor were conducted with an autoranging picoammeter (Keithley 485) equipped with a data logger (PASCO Xplorer GLX PS-2002), and the samples were put on a heating stage during electrical measurements. Figure 3a shows the picture of the as-fabricated SnO$_2$ gas sensor; the upper patterned SnO$_2$ film is on the PU nanospikes, and the lower patterned SnO$_2$ film is on a smooth PU surface.

3. Results and discussion

The morphologies of the as-fabricated SnO$_2$ thin film gas sensors on PU nanospikes were analyzed using a field emission scanning electron microscope (FESEM) (JOEL JSM-7401F) equipped with an energy-dispersive X-ray spectrooscope (EDX). A typical FESEM image of the SnO$_2$-coated PU nanospikes is shown in Figure 3b. The average diameter of the nanospikes is about 300 nm, and the lengths of them are about 600 nm which are in accordance with that of the as-fabricated silicon nanospikes [15] considering the thickness of the coated SnO$_2$ thin film. We can see that the SnO$_2$ thin film has a rough surface with many smaller gibbosity structures. The EDX data indicates that the SnO$_2$ film forms on the PU nanospikes.

The CO gas response curves of the SnO$_2$ thin film gas sensors fabricated on PU nanospikes and smooth PU surface were obtained through electrical measurement with an applied voltage of 1.5 V at room temperature, which are shown in Figure 4. During the measurements, the concentration of the CO gas is about 12.5 ppm (parts per million). The sensor resistance was determined by measuring the current going through the sensor. The sensitivity ($S$) of the sensor is defined as $S = R_0 / R_{gas}$, where $R_0$ is the sensor resistance without CO gas and $R_{gas}$ is the resistance measured under CO gas. For the normal SnO$_2$ thin films gas sensor fabricated on smooth PU surface, no visible response has been
Figure 3. (a) Photo of an as-fabricated SnO$_2$ gas sensor on PU nanospikes (upper) and on a smooth surface (lower). (b) FESEM image of as-fabricated thin film gas sensor on PU nanospikes coated with about 150 nm thick SnO$_2$ thin film.

measured in CO gas. This is in agreement with the previous results that the SnO$_2$ thin film sensor works in CO gas at high temperature. However, for the SnO$_2$ sensor fabricated on PU nanospikes, we can observe a significant increase of the current with increasing CO gas concentration due to the decrease of sensor resistance. The current of the SnO$_2$ sensor increases from about 610 nA to 775 nA with an increase of about 27%, which determines the sensitivity (about 1.27 at 12.5 ppm CO gas) of the SnO$_2$ sensor with a response time of about 100 s. This result indicates that the SnO$_2$ sensor fabricated on nanospikes has a competitive sensitivity even at room temperature.

In this phenomenon, the nanospike structures should be the key factor for enhancing the sensitivity of SnO$_2$ sensitive layer at room temperature. In the experiment, the nanospikes all have large area-on-volume ratio, so they have larger surface than the smooth substrates. The SnO$_2$ thin film is coated on the surface of PU nanospikes and also forms many smaller gibbosity structures as we have seen in the SEM picture (Figure 3b). Furthermore, it is well-known that the C-O is polarized with positive charges on oxygen atom and negative charges on carbon atom [24–26]. When the SnO$_2$ sensitive layer carries an electrical current, more electrons may accumulate on the tips of the nanospikes and the gibbosity structures to maintain the same electric potential on the surface, which results in strong local electrical fields around the sharp sites on the SnO$_2$ sensitive layer. Then more CO molecules will be pulled onto the tips of the SnO$_2$ layer and this will enhance the sensitivity of the SnO$_2$ thin film sensor.
The SnO2 thin film gas sensors were also fabricated on silicon nanospikes, and the fabrication procedure was reported in our previous papers [15]. The CO gas response curves of the SnO2 thin film gas sensors fabricated on silicon nanospikes and smooth silicon surface were obtained through electrical measurement with an applied voltage of 1.5 V on a heating stage, which are shown in Figure 5. During the measurements, the concentration of the CO gas was about 12.5 ppm and the temperature of the heating stage was about 500 K.

From the CO gas response curves in Figure 5, significant increases of the currents with about 33% (from 15 \( \mu \text{A} \) to 20 \( \mu \text{A} \)) and 19% (from 10.5 \( \mu \text{A} \) to 12.5 \( \mu \text{A} \)) can be observed for the SnO2 thin film gas sensors fabricated on silicon nanospikes and smooth surface, respectively. Obviously, the sensitivity of the SnO2 thin film gas sensors fabricated...
on silicon nanospikes is more than that of the SnO$_2$ thin film gas sensors fabricated on smooth surface. However, the response time of the SnO$_2$ thin film gas sensors fabricated on silicon nanospikes is also larger.

In this paper, for all CO gas response curves of SnO$_2$ thin films on PU substrate measured at room temperature and on silicon substrates measured at about 500 K, the currents increase with increasing CO gas concentration. However, in our previous work [15] about the SnO$_2$ thin film gas sensors fabricated on silicon nanospikes, the currents decrease as the concentration of CO increases at room temperature. Generally, the reducing gas such as CO will increase the conductivity of the SnO$_2$ sensitive layer because SnO$_2$ is usually regarded as an oxygen-deficient n-type semiconductor. In our previous work, the Sn thin films were heated at 500°C in air for 5 h and oxidized more adequately, so there were not much electrons on the surface. At room temperature in the CO gas, the carbon atoms with negative charges will be absorbed on the surface because the large size of the carbon atoms, so the negative field will decrease the current going through the n-type SnO$_2$ layer. When the gas sensor was heated at about 500 K, the oxygen atom in the SnO$_2$ layer near the surface might be detached and more electrons accumulate on the surface. So the oxygen atoms with positive charges will be absorbed on the surface, and positive field will increase the currents in the SnO$_2$ thin films. For the sensors fabricated on the PU substrates, the Sn thin films were heated at 250°C in air for 3 h and oxidized not very adequately. The electrons accumulated surface will absorb the oxygen atoms with positive charges, so the currents will also increase. In order to clearly understand the mechanism in this process, we still need further detailed studies.

By depositing a silane monolayer on the surface of the sensors with the PFOTS, which has low surface energy, we have also made the nanostructure sensor surface behave like self-cleaning lotus leaves [27]. The CO gas response sensitivity of the PFOTS-coated SnO$_2$ sensors is almost the same to that of the as-fabricated SnO$_2$ sensors without the PFOTS coating. The contact angle measurement conducted on the PFOTS monolayer-coated SnO$_2$ gas sensors indicates that a super-hydrophobic surface formed on the nanospike sensor. Dusts, which would disturb the performance of the sensor, will not stick on the surface strongly and can be easily swept away by water droplets, which will roll down the super-hydrophobic surface. The self-cleaning process does not obviously affect the performance of the SnO$_2$ sensor. Such a super-hydrophobic surface can protect the sensors exposed to moisture and heavy particulates, and can perform cleaning-in-place operations to prolong the lifetime of the sensors.

4. Conclusion

In conclusion, we have fabricated and measured the room temperature SnO$_2$ thin-film gas sensor with high sensitivity on the PU polymer nanospikes, which are replicated by the soft nanolithography method. A significant response to CO gas can be observed at room temperature. The electrical measurements show that the current of the SnO$_2$ gas sensor increases about 27% with the CO gas of about 12.5 ppm. The nanospike structures enhance the sensitivity of SnO$_2$ sensitive layer at room temperature due to the large area-on-volume ratio of the nanospikes. It demonstrates that the highly sensitive, repeatable and low-cost sensing systems can be easily fabricated by using the nanospike structures formed by femtosecond laser irradiation and the soft nanolithography.

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