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Satyajit Shukla

University of Central Florida

Peng Zhang

University of Central Florida

Hyoung J. Cho

University of Central Florida

Zia Rahman

University of Central Florida

Christina Drake

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Authors

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Hydrogen-discriminating nanocrystalline doped-tin-oxide room-temperature microsensor

Satyajit Shukla,^{a)} Peng Zhang, Hyoung J. Cho, Zia Rahman, Christina Drake, and Sudipta Seal^{b)}

Surface Engineering and Nanotechnology Facility (SNF), Advanced Materials Processing and Analysis Center (AMPAC) and Mechanical Materials Aerospace Engineering (MMAE) Department, Engineering 381, 4000 Central Florida Boulevard, University of Central Florida, Orlando, Florida 32816

Valentin Craciun

Materials Science and Engineering, 100 Rhines Hall, University of Florida, P.O. Box 116400, Gainesville, Florida 32611

Lawrence Ludwig

Electronics and Data Acquisition Laboratory, Kennedy Space Center (KSC), National Aeronautics and Space Administration (NASA), Florida 32899

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Highly hydrogen (H_2)-selective [relative to carbon monoxide (CO)] sensor, operating at room temperature, has been fabricated using the micronanointegration approach involving the deposition of the nanocrystalline indium oxide (In_2O_3)-doped tin oxide (SnO_2) thin film on microelectromechanical systems device. The present microsensor exhibits high room-temperature sensitivity towards H_2 ($S=12\,700$); however, it is insensitive to CO at room temperature. In view of the different gas selectivity mechanisms proposed in the literature, it is deduced that the In_2O_3 doping, the presence of $InSn_4$ phase, the low operating temperature (room temperature), the mesostructure, the small sizes of H_2 and H_2O molecules, the bulky intermediate and final reaction products for CO, and the electrode placement at the bottom are the critical parameters, which significantly contribute to the high room-temperature H_2 selectivity of the present microsensor over CO. The constitutive equation for the gas sensitivity of the semiconductor oxide thin-film sensor, proposed recently by the authors, has been modified to qualitatively explain the observed H_2 selectivity behavior. © 2005 American Institute of Physics. [DOI: 10.1063/1.2132095]

I. INTRODUCTION

Nanocrystalline tin oxide (SnO_2)-based semiconductor thin film is a well-known gas sensor based on the resistance change mechanism. The gas-sensing mechanism involves the reaction of the reducing gas molecules with the chemisorbed oxygen species ($O_{2(ad)}$ or $O_{(ads)}^-$), which reduces the potential barrier between the particles by releasing the electrons to the conduction band of SnO_2 .¹ The gas sensitivity of the SnO_2 -based thin film is then determined by the ratio R_{air}/R_{gas} , where R_{air} and R_{gas} are the sensor resistances in air without and with the reducing gas, respectively.

The development of highly sensitive and hydrogen (H_2)-selective sensors operating at room temperature has been the area of active research in recent years due to the potential H_2 applications in the space, automotive, and power generation industries. Recently, we developed a highly H_2 sensitive room-temperature sensor based on the nanocrystalline indium oxide (In_2O_3)-doped SnO_2 thin film deposited on the microelectromechanical systems (MEMS) device.² Such a microsensor exhibits very high room-temperature H_2 sensitivity as high as 10^5 . However, the present microsensor has not been tested for H_2 selectivity, and hence, this has been a prime motivation for the present investigation. In the litera-

ture, the H_2 selectivity, typically over carbon monoxide (CO), for the SnO_2 -based sensors has been demonstrated by others.^{3–7} However, all these earlier investigations show the H_2 selectivity over CO only in the higher operating temperature range ($>150\text{ }^\circ\text{C}$). On the other hand, in this investigation, we demonstrate the H_2 selectivity over CO in the lower operating temperature range ($<150\text{ }^\circ\text{C}$), typically at room temperature (which indicates a major cost savings in terms of energy). Interestingly, the room-temperature H_2 selectivity over CO observed for the present microsensor is much higher than those reported by some of the earlier investigations in the higher operating temperature region.^{3–5} As a result, we systematically study the room-temperature H_2 - and CO-sensing characteristics of the present microsensor within the air-pressure range of 50–600 Torr and explain the observed room-temperature H_2 selectivity over CO based on the different H_2 selectivity mechanisms available in the literature.^{3,6–13} We also modify the constitutive equation for the gas sensitivity of semiconductor oxide thin-film sensor, as proposed recently by the authors,^{14–16} to elucidate the room-temperature H_2 selectivity of the present microsensor over CO.

II. EXPERIMENT

A. Chemicals

Tin(IV)-isopropoxide ($Sn[OC_3H_7]_4$) (10 w/v %) in isopropanol (72 vol %), toluene (18 vol %), and indium(III)-

^{a)}FAX: (407)882-1462; electronic mail: sshukla@ucf.edu

^{b)}Author to whom correspondence should be addressed; FAX: (407)882-1462; electronic mail: sseal@mail.ucf.edu

FIG. 1. A silhouette of the MEMS device, with an interdigitated Au electrode configuration having the electrode distance of $20\ \mu\text{m}$, which is shown wire bonded to the integrated circuit (IC) chip after depositing the In_2O_3 -doped SnO_2 thin film via sol-gel dip-coating process. (i) IC chip, (ii) MEMS device, (iii) interdigitated Au electrodes, (iv) Au pad, and (v) resistive temperature sensor.

isopropoxide ($\text{Sn}[\text{OC}_3\text{H}_7]_3$) were purchased from Alfa Aesar (USA) and used as received. The MEMS devices were prepared as described below and utilized for the subsequent sol-gel dip-coating experiments.

B. Sensor fabrication

The entire sensor fabrication process has already been described elsewhere.² In short, the MEMS device, which utilizes oxidized Si wafer and Pyrex glass slide as the platforms, is patterned with four interdigitated gold (Au) electrodes and one temperature sensor, Fig. 1, using the thermal evaporation, photolithography, and wet chemical etching techniques. The gap between the Au electrodes is maintained at $20\ \mu\text{m}$.

The tin-isopropoxide solution in isopropanol and toluene, corresponding to the concentration of $0.23M$ of tin-isopropoxide, was used with the addition of calculated amount of indium(III)-isopropoxide to obtain the thin films of SnO_2 -6.5 mol % In_2O_3 via a dip-coating process. The coated MEMS devices were dried at $150\ ^\circ\text{C}$ for 15–30 min in air. The dip-coating and drying were repeated to obtain a desired film thickness. The dried gel films were sputtered with a thin Pt layer for 10 s using a sputter coater (K350, Emitech Ltd., Ashford, Kent, England). Finally, the Pt-sputtered dried gel films were fired at 400, 500, and $600\ ^\circ\text{C}$ in air for 1 h and utilized for the characterization of the coated MEMS devices.

The coated MEMS device calcined at $400\ ^\circ\text{C}$ was wire bonded to an integrated circuit chip, Fig. 1, and installed in the 32-pin socket assembly, which was in turn placed and centered over the sensor test board designed using LPKF CIRCUITCAM 4.0 software and cut using the LPKF BOARDMASTER 4.0 software on a single-sided copper clad prototype boards. Ultraviolet (UV) light-emitting diode (LED) lamp (which emits a band of visible light that peaks at 375 nm) was positioned 3 cm away from the packed MEMS device to facilitate the stimulation of the sensor surface with the UV radiation.

Two types of sensor devices were used for the sensor testing. One of the two sensors was a fresh sensor, which was not exposed previously to the UV radiation and was also not utilized to sense any reducing gases. The second one was an aged sensor (almost one year old and it was used to test the robustness of the sensor), which was occasionally exposed to the UV radiation during the H_2 -sensing tests. The room-temperature H_2 -sensing test results, obtained using the aged device, have been reported elsewhere.²

C. Characterization of Pt-sputtered In_2O_3 -doped SnO_2 thin-film sensor

Focused ion-beam (FIB, 200 TEM, FEI Company, Hillsboro, Oregon) milling was performed on the fresh In_2O_3 -doped SnO_2 thin film calcined at $400\ ^\circ\text{C}$ for the transmission electron microscopy (TEM) sample preparation. The procedure for the TEM sample preparation via FIB-milling technique has been described in detail elsewhere^{2,17} and was adopted in the present investigation. In short, the FIB-milling procedure involved sputtering of the 100-nm-thick Au–Pd layer followed by the local deposition of (1–2)- μm -thick Pt layer over the In_2O_3 -doped SnO_2 thin film in order to protect the thin film from getting destroyed during the FIB-milling operation. High-resolution TEM (HRTEM, FEI-Philips Tecnai F30) was then used to measure the film thickness and to determine the nanocrystallite size within the thin film. Various layers observed in the FIB-milled TEM sample are identified using the energy dispersive x-ray (EDX) analysis.

Glancing angle (1°) x-ray-diffraction (XRD) (Philips MRD X'Pert system) analysis was carried out to determine the crystalline phases present in the calcined thin films. Moreover, x-ray reflectance (XRR) analysis was carried out using X'Pert MRD in order to determine the thin-film density (that is, the amount of film porosity). The thin films calcined at 400 and $500\ ^\circ\text{C}$ were utilized for this purpose.

D. H_2 - and CO-sensing tests at room temperature

All H_2 and CO gas-sensing tests were conducted in the dynamic test condition at room temperature ($22\ ^\circ\text{C}$ with the relative humidity of 35%–50%) as described elsewhere.² In this type of sensor testing, the air pressure within the test chamber was reduced and maintained at a desired level using the turbo pumps. A mixture of appropriate amounts of nitrogen (N_2) and H_2 (or CO) was admitted into the test chamber through the respective mass-flow controllers. The N_2 (15 000 ppm) was used as a carrier gas. The amount of H_2 (or CO) in ppm was calculated using the ratio of the number of moles of H_2 (or CO) admitted into the test chamber per minute to the total number of moles of the gas molecules [that is, the summation of number of moles of N_2 , H_2 (or CO), and air] within the test chamber. Thus, in the dynamic test condition, a desired amount of H_2 (or CO) was continuously blown into the test chamber per minute and simultaneously pumped out of the test chamber throughout the test duration. Thus, the dynamic test condition simulates the condition, which may be encountered in an actual service application [for example, H_2 (or CO) leakage through a pipe line].

Single- as well as multicycle sensor tests were conducted with and without the UV-radiation exposure. In single-cycle sensor tests, 900 ppm of H_2 (or CO) were admitted into the test chamber under the dynamic test condition after stabilizing the initial sensor resistance in air. The total gas (H_2 or CO) exposure time was kept constant at 3600 s. Subsequently, air at 760 Torr was blown in to recover the initial sensor resistance. Single-cycle sensor tests for CO were carried out within the air-pressure range of 50–600 Torr to investigate the effect of air pressure on the room-temperature CO sensitivity of the present microsensor. Multicycle sensor tests were conducted only for H_2 . In this type of sensor test, the total H_2 exposure time was kept constant at 300–350 s, which was followed by air purge at 760 Torr to recover the initial sensor resistance in air; the cycle was then repeated five more times. During both single- and multicycle sensor tests, the sensor resistance is measured continuously after the time interval of 50 s. The choice of the sensor device (aged or fresh) for the sensor tests was for convenience and has been specified wherever necessary.

III. RESULTS

A. Thin-film morphological and structural analysis

1. HRTEM analysis

A typical TEM image of the FIB-milled sample, showing the cross section of the coated MEMS device, is presented in Fig. 2(a), where six distinct layers are identified using EDX. The first three layers correspond to silicon (Si), silica (SiO_2), and Au (pad), which originate from the as-fabricated MEMS device. The fourth layer is the In_2O_3 -doped SnO_2 thin film with a thickness of 125–150 nm. The fifth and the sixth layers, Fig. 2(a), correspond to Au–Pd and Pt, which originate from the FIB-milling procedure.

A typical HRTEM image, obtained from the region close to the interface of the Au pad and the In_2O_3 -doped SnO_2 sensing layer is presented in Fig. 2(b). An additional intermediate Cr layer (10 nm thick) is visible at the interface, which is not observed at low magnification, Fig. 2(a). This Cr layer also originates from the MEMS-device fabrication process and appears to be highly crystalline in nature. Lattice fringes can also be clearly observed within the In_2O_3 -doped SnO_2 layer, which suggest the crystalline nature of the thin-film sensor. The selected-area electron-diffraction (SAED) pattern obtained from the sensing layer is presented as an inset in Fig. 2(b). Sharp and continuous rings observed in the SAED pattern further support the highly nanocrystalline nature of the sensing layer. The average nanocrystallite size of In_2O_3 -doped SnO_2 layer appears to be extremely small within the range of 1–3 nm.

2. Glancing angle XRD analysis

Typical room-temperature glancing angle XRD (GAXRD) spectra, within the 2θ range of 10° – 80° , obtained using the In_2O_3 -doped SnO_2 thin-film sensor calcined at 400, 500, and 600 $^\circ C$ are presented in Fig. 3. After the calcination treatment at 400 $^\circ C$, Fig. 3(a), the thin-film sensor appears to be amorphous. However, this is in contradiction to the HRTEM analysis, where the presence of lattice fringes (1–3 nm

FIG. 2. Typical HRTEM images of FIB-milled TEM sample, at low (a) and high (b) magnifications, obtained from the In_2O_3 -doped SnO_2 thin-film sensor deposited on the MEMS device. In (a), (i) Si substrate, (ii) thermally grown SiO_2 , (iii) Au pad, (iv) In_2O_3 -doped SnO_2 , (v) Au–Pd, and (vi) Pt. In (b), (i) Au pad, (ii) Cr, and (iii) In_2O_3 -doped SnO_2 . An intermediate 10 nm Cr layer observed in (b) is not visible at low magnification in (a). The SAED pattern obtained from the In_2O_3 -doped SnO_2 region is shown as an inset in (b).

size) and the SAED pattern suggest the nanocrystalline nature of the thin-film sensor. It appears that the present thin-film sensor is electron crystalline but x-ray amorphous.

Further, after the calcination treatment at 500 $^\circ C$, Fig. 3(b), sharp as well as broad x-ray peaks have been noted, which suggest the crystallization of the x-ray amorphous thin film as a result of the calcination treatment at 500 $^\circ C$. The broad peak pattern observed in Fig. 3(b) also indicates the nanocrystalline nature of the thin-film sensor. It appears that the small nanocrystallites (1–3 nm) present after the calcination treatment at 400 $^\circ C$, Fig. 2(b), possibly act as nuclei for the phase evolution observed in Fig. 3(b). Interestingly, the peaks labeled in Fig. 3(b) do not correspond to the SnO_2 but match with that of the hexagonal $InSn_4$ (JCPDS File No. 07-0396). The remaining peaks in Fig. 3(b), however, corre-

FIG. 3. Typical GAXRD (1°) spectra obtained from the In_2O_3 -doped SnO_2 thin-film sol-gel dip coated on the MEMS device and calcined at different temperatures: (a) 400, (b) 500, and (c) 600 $^\circ\text{C}$. In (b) and (c), the peaks corresponding to the hexagonal InSn_4 (JCPDS File No. 07-0396) and tetragonal SnO_2 (JCPDS File No. 41-1445) have been indexed, respectively.

spond to the tetragonal SnO_2 and are labeled in Fig. 3(c) (JCPDS File No. 41-1445). Thus, both the hexagonal- InSn_4 and tetragonal- SnO_2 phases have been crystallized after the calcination treatment at 500 $^\circ\text{C}$. The hexagonal InSn_4 , however, gets transformed completely to tetragonal SnO_2 after the calcination treatment at 600 $^\circ\text{C}$, Fig. 3(c).

Typical XRR spectra acquired from the In_2O_3 -doped SnO_2 thin-film sensor calcined at 400 and 500 $^\circ\text{C}$ are presented in Fig. 4(a), while an enlarged view of the marked portion is shown in Fig. 4(b). The acquired spectra have been modeled using the Philips WINGX software package. In Fig. 4(b), the critical angle for the total x-ray reflection is observed to increase with increasing calcination temperature. Since the critical angle is proportional to the square root of the film density,^{18–20} this suggests that the amount of film porosity decreases with increasing calcination temperature. The thin films calcined at 400 and 500 $^\circ\text{C}$ contain 48% and 30% porosity, respectively.

FIG. 4. Typical XRR spectra (a) acquired from the In_2O_3 -doped SnO_2 thin-film sol-gel dip coated on the MEMS device and calcined at different temperatures: (i) 400 $^\circ\text{C}$ and (ii) 500 $^\circ\text{C}$. The magnified view of the marked portion in (a) is presented in (b).

FIG. 5. Typical multicycle sensor tests conducted using the fresh sensor for detecting H_2 at room temperature under the dynamic test condition. In (a) and (b), the response time is kept constant at 300–350 and 3600 s, respectively. Both sensor tests are conducted for 900 ppm H_2 without the UV-radiation exposure. The data points are separated by 50 s time interval.

B. H_2 and CO sensing at room temperature

1. Multicycle H_2 -sensing test

Typical multicycle H_2 -sensing test results obtained using the fresh sensor (calcined at 400 $^\circ\text{C}$) for the total response time of 300–350 and 3600 s are presented in Figs. 5(a) and 5(b), respectively. In Fig. 5(a), the sensor resistance is initially stabilized in air without the UV-radiation exposure at 10–50 Torr air pressure. An introduction of 900 ppm H_2 results in a quick drop in the sensor resistance (note that all data points in Fig. 5 are separated by the time interval of 50 s). After a response time of 300–350 s, the sensor resistance is recovered quickly by blowing the air at 760 Torr into the test chamber. Six cycles have been presented, which suggest the reproducibility of the present fresh sensor. In Fig. 5(b), the total gas exposure time is extended to 3600 s. It is observed that, during the long exposure to H_2 , the rate of drop in the sensor resistance decreases with time and the sensor resistance stabilizes in the presence of H_2 after a particular time interval. Interestingly, the sensor resistance stabilizes earlier in the second cycle than in the first cycle. The total drop in the sensor resistance, as large as three to four orders of magnitude, has been noted, Fig. 5(b), after the total response time of 3600 s.

2. Single-cycle H_2 - and CO-sensing tests

Single-cycle H_2 and CO sensor tests were conducted under the dynamic test condition, with and without the UV-

FIG. 6. Typical variation in the room-temperature sensor resistance of the aged sensor, as a function of time, after exposure of the sensor surface to the UV radiation in air at 50 Torr air pressure.

radiation exposure, at 50 Torr air pressure and 22 °C, and using the aged sensor calcined at 400 °C. The aged sensor was initially exposed to the UV radiation, which results in the decrease in the sensor resistance, Fig. 6. Immediately after the UV exposure, the sensor resistance drops rapidly from 200 to 20 MΩ. This is followed by a gradual decrease in the sensor resistance from 20 to 6 MΩ over the period of 21 h. Comparison with the previously reported results² shows that the original resistance of the aged sensor at 50 Torr air pressure, without the UV radiation, has been drifted from 2 GΩ to 200 MΩ over the period of one year.

After the complete stabilization of the sensor resistance under the UV radiation at 50 Torr air pressure and at room temperature, single-cycle H₂- and CO-sensing tests were conducted. As observed in Fig. 7(a), for the total gas expo-

FIG. 7. Typical variation in the room-temperature sensor resistance of the aged sensor as a function of time (a) in the presence of 50 Torr air containing 900 ppm of H₂ and CO. The sensor tests are conducted under the dynamic test condition at room temperature under the UV radiation. The total gas exposure time is kept constant at 3600 s. In (b) is an enlarged view of the sensor tests conducted for 900 ppm CO.

sure time of 3600 s, an introduction of 900 ppm H₂ into the test chamber results in the rapid drop in the sensor resistance. The rate of drop in the sensor resistance, however, decreases with increasing gas exposure time. A total of two to three orders of magnitude decrease in the sensor resistance has been observed in Fig. 7(a) in the presence of H₂. On the contrary, an introduction of 900 ppm CO into the test chamber, under the dynamic test condition, hardly results in any change in the sensor resistance. An enlarged view of CO-sensing test result is shown in Fig. 7(b). For the total gas exposure time of 3600 s, the sensor resistance decreases from 8.3 to 6.9 MΩ in the presence of CO. In both H₂- and CO-sensing tests, the original sensor resistance is recovered rapidly after blowing the air at 760 Torr into the test chamber. Thus, the total drop in the sensor resistance, under the UV-radiation exposure, is observed to be substantially greater in the presence of H₂ than that in the presence of CO, which suggests that the present microsensor device exhibits higher room-temperature H₂ selectivity over CO under the UV radiation.

The room-temperature CO-sensing test results, under the UV radiation and at higher air pressures, specifically 200, 400, and 600 Torr, are presented in Figs. 8(a)–8(c), respectively. Even at higher air pressures, very small decrease in the sensor resistance has been noted after an introduction of 900 ppm CO into the test chamber, similar to the sensor behavior observed at 50 Torr air pressure, Fig. 7(b). The sensor resistance is recovered quickly after blowing the air at 760 Torr into the test chamber. This suggests that the present microsensor exhibits very low room-temperature CO sensitivity, under the UV radiation, within the air-pressure range of 50–600 Torr.

Without the UV radiation, the sensor resistance in air increases back gradually and tends to stabilize at its original value, Fig. 9, after 16 h. Typical H₂ and CO sensor test results obtained under the dynamic test condition without the UV radiation, at 50 Torr air pressure and 22 °C, are presented in Fig. 10(a). Similar to the previous case, Fig. 7(a), the sensor resistance decreases very rapidly with an introduction of 900 ppm H₂ into the test chamber. Comparison of Figs. 7(a) and 10(a) reveals that the sensor resistance in the presence of H₂ stabilizes earlier without the UV radiation than that under the UV radiation. In the presence of 900 ppm H₂, four orders of magnitude drop in the sensor resistance has been noted without the UV-radiation exposure, Fig. 10(a), which is larger than that observed with the UV radiation, Fig. 7(a). Moreover, the present microsensor hardly responds to 900 ppm CO within the total gas exposure time of 3600 s without the UV radiation. An enlarged view of CO-sensing test result, without the UV radiation, is presented in Fig. 10(b). A very small drop in the sensor resistance from 620 to 610 MΩ has been noted in the presence of CO.

IV. DISCUSSION

A. Synthesis of nanocrystalline In₂O₃-doped SnO₂ thin film

Nanocrystalline In₂O₃-doped SnO₂ thin films have been synthesized using the sol-gel process and deposited over the

FIG. 8. Typical variation in the room-temperature sensor resistance of the aged sensor, as a function of time, in the presence of 50 Torr air containing 900 ppm of CO. The sensor tests are conducted under the dynamic test condition at room temperature under the UV radiation at different air pressures: (a) 200, (b) 400, and (c) 600 Torr. The total gas exposure time is kept constant at 3600 s.

MEMS device, with the electrode distance of 20 μm , via a dip-coating process. The sequence of chemical reactions involved during the processing (film deposition, drying, and calcination) has already been described elsewhere.²¹ It is observed that, after the calcination treatment at 400 $^{\circ}\text{C}$, the thin-film sensor is composed of binary phases consisting the

FIG. 9. Typical variation in the room-temperature sensor resistance of the aged sensor, as a function of time, at 50 Torr air pressure after switching off the UV radiation.

FIG. 10. Typical variation in the room-temperature sensor resistance of the aged sensor as a function of time (a) in the presence of 50 Torr air containing 900 ppm of H_2 and CO. The sensor tests are conducted under the dynamic test condition at room temperature without the UV radiation. The total gas exposure time is kept constant at 3600 s. (b) Is an enlarged view of the sensor tests conducted for 900 ppm CO.

tetragonal SnO_2 doped with In_2O_3 and the hexagonal InSn_4 . The formation of hexagonal- InSn_4 phase is very surprising as its formation has not been reported in the literature. In the authors' view, the nucleation of this phase along with the tetragonal- SnO_2 nanocrystallites is beneficial to restrict the excessive grain growth of the latter. As a result, the nanocrystallite size as small as 1–3 nm could be obtained after the calcination at 400 $^{\circ}\text{C}$, which is favorable to enhance the H_2 sensitivity (and hence H_2 selectivity) of the present microsensor. Overall, the present SnO_2 -based thin-film sensor is a binary phase sensor and not a single phase sensor as generally reported in the literature. Due to the presence of higher amount of film porosity (48%) along with the smallest nanocrystallite size of 1–3 nm, the thin-film sensor calcined at 400 $^{\circ}\text{C}$ was an obvious choice for sensing H_2 at room temperature and to examine its room-temperature H_2 selectivity over CO.

B. Sensing H_2 at room temperature

1. Fresh sensor

The H_2 sensitivity, the response, and the recovery times for the fresh sensor are calculated for each cycle presented in Fig. 5(a). For the constant response time of 300–350 s, the H_2 sensitivity and the recovery time for the fresh sensor lie within the range of 138–230 and 150–200 s, respectively. Relatively higher room-temperature H_2 sensitivity with lower response and recovery times is very significant since the fresh sensor sensed H_2 at room temperature without any prior exposure to the UV radiation. Moreover, the observed room-temperature H_2 -sensing characteristics of the fresh sensor are quite satisfactory for all practical applications, which

FIG. 11. Typical variation in the room-temperature H_2 sensitivity of the fresh sensor, as a function of time, derived using Fig. 5(b). The total gas exposure time is kept constant at 3600 s. The sensor test is conducted for 900 ppm H_2 without the UV radiation exposure. The data points are separated by 50 s time interval.

require a room-temperature H_2 sensor with subsequent energy savings. As shown in Fig. 11 [which is obtained using Fig. 5(b)], the fresh sensor exhibits the maximum H_2 sensitivity of 1800 and 2200 for the first two cycles, respectively, with the response time of 2600 and 1800 s and the recovery time of 950 and 800 s, respectively. The fresh sensor, thus, shows enhanced room-temperature H_2 sensitivity with reduced response and recovery times in the second cycle relative to those in the first cycle, which is consistent with our earlier investigation.²

2. Aged sensor

The variation in the room-temperature H_2 sensitivity of the aged sensor as a function of the gas exposure time, with and without the UV radiation, derived using Figs. 7(a) and 10(a) is presented and compared in Fig. 12. It is clear from Fig. 12 that, similar to the behavior of the fresh sensor (Fig. 11), the room-temperature H_2 sensitivity of the aged sensor tends to attain the saturation level well ahead of the total gas exposure time of 3600 s for both with and without the UV radiation. The maximum room-temperature H_2 sensitivity of 380 and 12 700 has been observed with and without the UV

FIG. 12. Comparison of the variation in the room-temperature H_2 sensitivity of the aged sensor, as a function of time, with (i) [derived using Fig. 7(a)] and without (ii) [derived using Fig. 10(a)] the UV-radiation exposure. The sensor tests are conducted for 900 ppm H_2 with the total gas exposure time kept constant at 3600 s. The data points are separated by 50 s time interval.

FIG. 13. Schematic presentation of the procedure utilized to determine the room-temperature H_2 sensitivity and the response time of the aged sensor. The procedure is applied to the sensitivity-time curves presented in Fig. 12.

radiation, respectively, with the recovery time of 780 and 1050 s, respectively. The maximum room-temperature H_2 sensitivity of the aged sensor is noted to be two orders of magnitude greater without the UV radiation than that with the UV radiation, which is also consistent with our previous analysis.² The degradation of the room-temperature H_2 sensitivity of the aged sensor under the UV radiation has been attributed to the reduced sensor resistance (Fig. 6) as a result of desorption of the surface-adsorbed oxygen ions due to the UV-radiation exposure.² As reported earlier,² the aged sensor exhibited the maximum room-temperature H_2 sensitivity of 10^5 , which is an order of magnitude larger than that obtained ($S=12\,700$) by testing the aged sensor after a gap of one year. This degradation in the performance of the aged sensor, over the period of one year, has been attributed to the drift in its original sensor resistance in air. The current maximum room-temperature H_2 sensitivity of the old sensor is, however, still large enough for any practical application.

Since the sensor tests for the short duration [similar to the one conducted for the fresh sensor, Fig. 5(a)] are not performed for the aged sensor, the room-temperature response time and the corresponding H_2 sensitivity values (suitable for practical purposes) are obtained using the procedure as described in Fig. 13. The dotted lines $Y'Y$ and $X'X$ are the extensions of the linear part of the sensitivity-time curve, which intersect each other at a point through which a line $Z'Z$ is drawn parallel to Y axis, which in turn intersects the sensitivity-time curve at point w . The response time and the room-temperature H_2 sensitivity of the aged sensor are determined with respect to the point w .

With this definition, the response time of the aged sensor has been calculated (using Fig. 12) to be 600 and 300 s with the corresponding room-temperature H_2 sensitivities of 80 and 2000 with and without the UV-radiation exposure, respectively, which are suitable for all practical applications requiring a room-temperature H_2 sensor. Comparison of Figs. 5(a), 11, and 12 reveals that, for the same response time of 300–350 s, the aged sensor exhibits higher room-temperature H_2 sensitivity, by more than one order of magnitude, relative to that of the fresh sensor without the UV-

FIG. 14. Comparison of the variation in the room-temperature CO sensitivity of the aged sensor, as a function of time, with (i) [derived using Fig. 7(a)] and without (ii) [derived using Fig. 10(a)] the UV-radiation exposure. The sensor tests are conducted for 900 ppm CO with the total gas exposure time kept constant at 3600 s.

radiation exposure. Moreover, the maximum H_2 sensitivity is also larger for the aged sensor relative to that of the fresh sensor without the UV exposure. It appears that the prior exposure to the UV radiation possibly sets favorable conditions for achieving higher room-temperature H_2 sensitivity. It has been demonstrated that²² the exposure to the UV radiation burns the organic residues present on the sensor surface, and as a result, much cleaner surface is made available for the surface adsorption of large amount of oxygen ions. In addition to this, although demonstrated at higher temperature, exposure to H_2 gas causes a change in the morphology of the semiconductor oxide surface making it more fibrous and porous.²³ These factors, which may be associated only with the aged sensor, have been attributed for its larger room-temperature H_2 sensitivity relative to that of the fresh sensor, which has no prior history of UV-radiation and H_2 exposures.

C. Sensing CO at room temperature (aged sensor)

The obtained variation in the room-temperature CO sensitivity, derived using Figs. 7(b) and 10(b) as a function of the gas exposure time, is presented in Fig. 14. For the total gas exposure time of 3600 s, the present microsensor exhibits the CO sensitivities of 1.20 and 1.02 (very negligible for any practical applications) with and without the UV-radiation exposure, respectively. The present microsensor is, thus, almost insensitive to CO at room temperature under both conditions although higher CO sensitivity has been noted under the UV radiation than that without the UV radiation. The room-temperature CO sensitivity values observed for the present microsensor are, however, comparable with those reported by others for the SnO_2 -based sensors.^{24–27} The room-temperature CO sensitivity reported in the literature lie within the range of 1.02–1.90 for the CO concentration levels of 50 ppm–1 vol %.^{24–26} Moreover, within the higher operating temperature range of 100–600 °C, the SnO_2 -based sensors exhibit CO sensitivity of 1.2–100 for the CO concentration levels of 50–500 ppm.^{5,28–30} Thus, the room-temperature H_2 sensitivity of the present SnO_2 -based microsensor is substantially higher than its room-temperature (as observed in this investigation and reported earlier by others^{24–26}) as well as high-temperature CO

FIG. 15. Comparison of the variation in the room-temperature H_2 and CO sensitivity of the aged sensor, as a function of time, with (a) [derived using Fig. 7(a)] and without (b) [derived using Fig. 10(a)] the UV-radiation exposure. The sensor tests are conducted under the dynamic test condition, at 50 Torr air pressure, for 900 ppm of H_2 and CO. The total gas exposure time is kept constant at 3600 s.

sensitivities.^{5,28–30} This suggests that the present microsensor is H_2 selective over CO at room temperature.

D. Room-temperature H_2 selectivity over CO (aged sensor)

In Figs. 15(a) and 15(b), we compare the variation in the room-temperature H_2 sensitivity of the present microsensor with its room-temperature CO sensitivity as a function of the gas exposure time, observed with and without the UV radiation, respectively. It is evident that under both test conditions, the present microsensor is highly H_2 selective over CO at room temperature. By defining the H_2 selectivity over CO as the ratio of its H_2 sensitivity to CO sensitivity (at the same operating temperature), the H_2 selectivities of 317 and 12 450 have been calculated, at room temperature, for the present microsensor with and without the UV radiation, respectively. The H_2 selectivity over CO is, thus, observed to be larger without the UV radiation than that with the UV radiation. In the literature, the H_2 selectivity over CO, within the range of 4–36 000, has been reported within the temperature range of 150–350 °C.^{3–7} However, all these investigations report the H_2 selectivity over CO well above the room temperature. In contrary, we demonstrate here the H_2 selectivity over CO at room temperature.

1. In view of H_2 selectivity mechanisms

Various mechanisms, such as work function,⁸ temperature modulation,⁹ O_2 partial pressure,³ surface functionalization,^{6,7} doping,^{3,4} molecular sieves,^{10,11,31} and mesostructures,^{5,12,13} have been demonstrated in the litera-

ture to achieve the H_2 selectivity over other reducing gases (typically CO). All these H_2 selectivity mechanisms are considered below to recognize the factors that may affect the room-temperature H_2 selectivity of the present microsensor.

It has been observed that the work function of SnO_2 changes with time in the presence of H_2 .⁸ In the lower operating temperature range (50–150 °C), the work function of SnO_2 has been observed to increase with time, while in the higher operating temperature range (200–250 °C), it has been noted to decrease. It has been suggested that⁸ in the lower operating temperature range, $O_{2(ads)}^-$ is the major surface-adsorbed species, which reacts with H_2 to form hydroxyl ions (OH^-) on the sensor surface by capturing the electrons from the conduction band of SnO_2 ,

The trapping of electrons results in increased work function of the SnO_2 -based sensor. However, at higher operating temperatures, $O_{(ads)}^-$ is the major surface-adsorbed species, which readily reacts with the H_2 releasing the electrons to the conduction band as

which decreases the work function of the sensor. It has been proposed that⁸ by monitoring the changes in the work function of the sensor along with the changes in the sensor resistance, H_2 may be selectively detected in the presence of other reducing gases. In the present investigation, however, we do not monitor the changes in the work function of the sensor as a function of the gas exposure time. Interestingly, large decrease in the sensor resistance, observed in the presence of H_2 [Figs. 5(b), 7(a), and 10(a)] at room temperature, is in favor of the reaction presented in Eq. (2), which assumes the surface adsorption of O^- species.

In the “temperature-modulation” method, the sensor temperature is monitored during the reducing gas exposure. It has been observed that⁹ the drop in the sensor resistance, in the presence of a reducing gas such as H_2 , is accompanied by a drop in the sensor temperature. There are two competing processes which affect the sensor temperature in the presence of H_2 . First, the reaction between the H_2 and the surface-adsorbed oxygen ions is an exothermic reaction. As a result, this factor tends to increase the sensor temperature with the drop in the sensor resistance. However, the thermal conductivity of the SnO_2 sensor also increases in the presence of H_2 due to an increased charge-carrier density in the conduction band of SnO_2 . This second factor tends to decrease the sensor temperature with a drop in the sensor resistance. The exact sensor temperature is determined by an optimum balance between these two parameters. It is experimentally observed that⁹ for the H_2 concentration within the range of 10–500 ppm, the sensor temperature decreases; however, within the H_2 concentration range of 500–1000 ppm, the drop in the sensor temperature reduces continuously. Hence, in the lower H_2 concentration range, the effect of the increase in the thermal conductivity dominates the effect of an exothermic reaction, while in the higher H_2 concentration range, the effect of the latter dominates that

of the former. By monitoring the sensor temperature change (ΔT) along with the sensor resistance change (ΔR), it is possible to construct a two-dimensional map of ΔR and ΔT , which is useful in detecting the H_2 selectively and determining its concentration using a single SnO_2 -based sensor.⁹ Different gases have different curves in this two-dimensional space, and as a result, simultaneous measurements of sensor-resistance and sensor-temperature changes make an identification of H_2 possible relative to other gases. In the present investigation, however, the sensor temperature has not been measured as a function of the H_2 exposure time and no attempt has been made to construct a two-dimensional map of ΔR and ΔT to selectively sense H_2 over CO at room temperature.

It has been demonstrated that³ the SnO_2 -based sensor can be made H_2 selective in the presence of CO if operated at very low “ O_2 partial pressure” range (0.08–10 Torr), where the H_2 concentration in the atmosphere exceeds the O_2 concentration. Very high H_2 sensitivity ($S=70$ –2000) has been noted under these conditions relative to that of CO ($S=7$ –20). In addition to this, under the low O_2 partial pressures, the decrease in the sensor temperature associated with the gas sensing has been reported to be higher for H_2 than that with CO.³ Hence, by simultaneously monitoring the sensitivity and the temperature drop, typically at lower O_2 partial pressures, H_2 can be selectively detected in the presence of CO. Based on our previous work³² and the results obtained in this investigation, we demonstrate the room-temperature H_2 selectivity over CO within the air-pressure range of 50–600 Torr. Since the O_2 partial pressure, in this air-pressure range, varies within the range of 10–120 Torr,³² the room-temperature H_2 selectivity over CO at 50 Torr air pressure, as observed in this investigation, may be partly attributed to the low O_2 partial pressure of 10 Torr. However, as shown in Fig. 16(a), which is derived using Figs. 7(b) and 8, the present microsensor exhibits very low room-temperature CO sensitivity at higher air pressures (>50 Torr) as well. Comparison of the room-temperature CO sensitivity with the room-temperature H_2 sensitivity (as reported elsewhere³²), Fig. 16(b), within the air pressure range of 50–600 Torr reveals that the present microsensor exhibits higher room-temperature sensitivity to H_2 than CO within the selected air-pressure range. Hence, the present microsensor is highly room-temperature H_2 selective over CO within the entire investigated air-pressure range of 50–600 Torr. Since, except at 50 Torr air pressure, the O_2 partial pressure is greater than 10 Torr, the H_2 selectivity of the present microsensor over CO at higher air pressures (>50 Torr) has been certainly contributed by the factors other than the low O_2 partial pressure.

The “surface-functionalization” technique for achieving the H_2 selectivity involves altering the sensor surface with other metal oxide nanoparticles.^{6,7} H_2 -selective sensors have been synthesized by modifying the surface of pure SnO_2 (which is not H_2 selective in the pure form) with ruthenium oxide (RuO) and palladium oxide (PdO). It has been observed that, for the particular Ru/Pd ratio of 1.28, the sensor exhibits maximum H_2 sensitivity ($S=1350$) at 250 °C, while the sensitivity to other gases, such as CO ($S=0.08$), liquefied

FIG. 16. (a) Variation in the room-temperature CO sensitivity of the present microsensor as a function of air pressure within the range of 50–600 Torr. The sensor tests are conducted under the dynamic test condition for 900 ppm CO. The data are derived using Fig. 8. (b) Comparison of the room-temperature CO sensitivity ($\circ$) with the room-temperature H₂ sensitivity ($\bullet$) of the present microsensor as a function of air pressure within the range of 50–600 Torr. The variation in the room-temperature H₂ sensitivity as a function of air pressure has been reported earlier elsewhere (Ref. 32), but it is reproduced here for comparison purposes.

petroleum gas (LPG) ($S=375$), ammonia (NH₃) ($S=0.14$), nitrogen dioxide (NO₂) ($S=0.24$), and alcohol ($S=20.5$), is very low. Thus, the SnO₂-based sensor surface modified with RuO and PdO is H₂ selective over CO. Although the exact reasoning for an enhanced H₂ selectivity of pure-SnO₂ sensor, after the surface modification with RuO and PdO, is not yet known, it is believed that,^{6,7} the adsorption configuration and the surface fragmentation of gaseous molecules (typically H₂) on Ru and Pd sites may be responsible for the high H₂ selectivity over CO (and other reducing gases). In the present investigation, however, the surface-functionalization technique has not been utilized to achieve the desired room-temperature H₂ selectivity over CO.

In the “doping” mechanism, the H₂-selective SnO₂-based sensors have been developed by doping PdO and Bi₂O₃/Sb₂O₅ in SnO₂.³ Much higher sensitivity ($S=12$ and $S=7$ at 280 and 380 °C, respectively) for H₂ has been observed for these sensors relative to that for CO ($S<2$). Hence, the lattice doping with PdO and Bi₂O₃/Sb₂O₅ is one of the techniques, which may be adopted to produce H₂-selective sensors. Doping ZnO in CuO-doped SnO₂ has also been reported to be an efficient way to synthesize the H₂-selective sensor relative to CO with the H₂ selectivity of 5–6 at 350 °C.⁴ The H₂ selectivity for the doped SnO₂-based sensor has been suggested to be a result of the microstructural and the compositional effects produced by doping ZnO into CuO-doped SnO₂.⁴ In the present investigation, we dope In₂O₃ into SnO₂ and obtain the room-temperature H₂ selectivity over CO within the air-pressure range of 50–600 Torr.

In the “molecular-sieve” mechanism related to the H₂ selectivity, the secondary oxide layer (few tens of nanometers thick) is formed over the SnO₂-based sensor, which effectively allows only the H₂ in a gaseous mixture to diffuse in and contact the sensor surface.^{10,11,31} The H₂-selective sensors using the molecular-sieve approach has been synthesized based on “hot-wire-type” semiconductor gas sensor, which consists of a Pt-wire coil covered with a sintered porous bead of SnO₂ powder.¹¹ In order to achieve the H₂ selectivity, the surface layer of the porous SnO₂ bead is converted into a dense layer via accumulation of SiO₂ into the pores by chemical-vapor deposition (CVD) of hexamethyldisiloxane (HMDS). In other investigation,³¹ very thin (10 nm) SiO₂ layer has been sputtered over the SnO₂-based thin-film sensor. Gases such as H₂, H₂O, O₂, and CO have different molecular diameters, 0.218, 0.272, 0.296, and 0.380 nm, respectively, thus, H₂ has the smallest molecular diameter. As a result, the dense SiO₂ layer functions as a molecular sieve and allows selective H₂ diffusion, thus, resulting in prominent H₂ selectivity. The reducing gases, such as CO, with larger molecular diameters than H₂ are almost blocked due to an effective diffusion control by the surface SiO₂ layer. In the present investigation, the molecular-sieve approach has not been exploited for achieving the desired room-temperature H₂ selectivity over CO.

Rather than coating the sensor surface with a relatively thick SiO₂ film, another approach has been suggested¹⁰ to increase the H₂ filtering effect using the molecular sieve, which involves coating each individual SnO₂ nanocrystallite with very tiny (2–3 nm) SiO₂ particles. It has been observed that the H₂ sensors formed using these SiO₂-coated SnO₂ nanocrystallites exhibit enhanced H₂ sensitivity ($S=3530$) relative to that of uncoated-SnO₂ nanoparticles ($S=31$). Moreover, the H₂ sensitivity is also observed to be much higher than that for other gases such as CH₄ and C₃H₈ ($S<10$). It appears that the molecular-sieve approach appears to be a promising technique for achieving the high H₂ selectivity. In the present investigation, the surface coating of SnO₂ nanocrystallites with the secondary oxides has not been obtained to impart the desired H₂ selectivity over CO. However, we do observe the presence of hexagonal-InSn₄ phase within the tetragonal-SnO₂ thin-film sensor, which is equivalent of having the SiO₂ phase surrounding the SnO₂ particles. Hence, according to the authors, the presence of hexagonal InSn₄ surrounding the tetragonal-SnO₂ particles may possibly hinder the diffusion of large diameter CO molecules into the thin-film sensor, thus, effectively contributing to the room-temperature H₂ selectivity of the present microsensor by increasing the CO concentration gradient within the thin-film sensor.

“Mesosstructured” SnO₂ with pore size of 1–100 nm have also been observed to be highly H₂ selective relative to CO.^{5,12,13} Mesosstructured SnO₂ has been synthesized with high specific surface area (136–368 m²/g), small average nanocrystallite size (2–8 nm), and small pore diameter (2.2–4.0 nm) using a cationic surfactant [cetyltrimethylammonium bromide (CTAB)] as an organic template.¹³ Further, by mechanically mixing SnO₂ with Si–Al–MCM-41 [a synthetic material possessing very high surface area

(1200 m²/g) and very uniform mesoporous structure (3 nm pore diameter)] and treating the solid mixture at high temperatures, Si–Al–MCM-41-modified SnO₂ sensors have been prepared, which are highly H₂ selective relative to CO.¹² It is believed that the difference in the diffusion of H₂ and CO into the pore structures of SnO₂ plays an important role in enhancing the H₂ selectivity over CO. H₂, being smaller in size, is diffused much faster than the larger CO molecules, thus, accessing more SnO₂ surface area, resulting in high H₂ sensitivity and selectivity. In the present investigation, the thin film sensor has been synthesized via sol-gel dip-coating process. This thin-film synthesis process invariably results in the development of large amount of film porosity and/or cracks,²¹ which might be useful from the H₂ selectivity point of view. The present sensor, which is calcined at 400 °C, possesses 48% porosity. We assume here that its structure is comparable with the mesostructured SnO₂ reported in the literature as the H₂ selectivity over CO has been observed at room temperature. According to the authors, the difference in the diffusivity of H₂ and CO through this mesostructure is one of the major factors for achieving the room-temperature H₂ selectivity over CO using the present microsensor.

It, thus, appears that the combination of In₂O₃ doping, the presence of InSn₄ phase, the small nanocrystallite size (1–3 nm), the low O₂ partial pressure, and the mesostructure are the primary factors, which are responsible for the room-temperature H₂ selectivity over CO of the present microsensor. Interestingly, the presence of Pt catalyst, as utilized in this investigation, has been reported to favor the CO selectivity over H₂ within the temperature range of 150–350 °C.³³

2. In view of constitutive equation and related theories

Recently, the authors derived a constitutive equation for the gas sensitivity of nanocrystalline semiconductor oxide thin-film sensor based on a single-crystal model,^{14,15} which is then extended to two-dimensional thin-film sensor.¹⁶ The constitutive equation for the gas sensitivity (S_{tf}) of semiconductor oxide thin-film sensor is given by the relationship of the form

$$S_{\text{tf}} = \frac{A_1}{D} \sqrt{\frac{4\varepsilon_r\varepsilon_o k}{q^2} \frac{\sqrt{T}}{n_b^{1.5}}} C^m \exp\left[\frac{q^2}{2\varepsilon_r\varepsilon_o k} \left(\frac{[\text{O}^-]^2}{[V_o]T}\right)_{\text{avg}}\right], \quad (3)$$

where A_1 is a constant, D is the nanocrystallite size, $\varepsilon_r\varepsilon_o$ is a permittivity of the sensor, k is the Boltzmann constant, q is the electronic charge, T is the absolute temperature, n_b is the charge-carrier concentration within the bulk, C is the amount of the reducing gas (in ppm), m is the gas exponent, $[\text{O}^-]$ is

the occupied density of surface states, and $[V_o]$ is the oxygen-ion-vacancy concentration. In Eq. (3), the exponential term has been averaged over the entire film thickness. Further, the present model assumes that there exists a concentration gradient of the adsorbed oxygen ions within the thin-film sensor; however, no concentration gradient has been assumed for the reducing gas. As a result, the term C in Eq. (3) is assumed to be a constant. In the case of a thin-film sensor with mesostructures, the gas molecules diffuse into the pores by the Knudsen diffusion mechanism.^{34,35} The Knudson diffusion coefficient (D_k), under these conditions, is dependent on the operating temperature (T), pore radius (r), and molecular weight (M) of the diffusing gas as

$$D_k = \frac{4r}{3} \sqrt{\frac{2RT}{\pi M}}, \quad (4)$$

where R is a gas constant. For a given film thickness, the lower operating temperature and the larger molecular weight of the diffusing gas may lead to the large concentration gradient of the reducing gas within the thin-film sensor. The concentration of the reducing gas (A) within the thin-film sensor can be determined using the equation of the form³⁴

$$C_A = C_{A,s} \frac{\sinh(x\sqrt{k/D_k}) + \sinh[(2L-x)\sqrt{k/D_k}]}{\sinh(2L\sqrt{k/D_k})}, \quad (5)$$

where C_A and $C_{A,s}$ are the reducing gas concentrations within the thin film and at the film surface, respectively, k is the rate constant for the chemical reaction at the sensor surface, L is the film thickness, and x is the distance from the film surface. Equation (3) can be easily converted to³⁵

$$C_A = C_{A,s} \frac{\cosh[(L-x)\sqrt{k/D_k}]}{\cosh(L\sqrt{k/D_k})}. \quad (6)$$

It has been demonstrated that³⁴ the large value of $L(k/D_k)^{1/2}$ results in the large concentration gradient within the thin-film sensor while the smaller value gives a flat concentration profile. In the single-crystal model, which is extended to the two-dimensional thin film, if it is assumed that the concentration gradient exists for the reducing gas within the thin-film sensor, then the constitutive equation for the gas sensitivity of the semiconductor oxide thin-film sensor¹⁶ gets modified to

$$S_{\text{tf}} = A_1 \sum_{n=1}^N \frac{N}{1 + \{(2d/D)C^m \exp[(q^2/2\varepsilon_r\varepsilon_o k)([\text{O}^-]^2/[V_o]T)]\}_n}. \quad (7)$$

Substituting Eq. (6) in Eq. (7) we get

$$S_{\text{tf}} = A_1 \sum_{n=1}^N \frac{N}{1 + \{(2d/D)(C_{A,s}\{\cosh[(L-x)\sqrt{k/D_k}]/\cosh(L\sqrt{k/D_k})\})^m \exp[(q^2/2\varepsilon_r\varepsilon_o k)([\text{O}^-]^2/[V_o]T)]\}_n}. \quad (8)$$

The modified constitutive equation, Eq. (8), for the gas sensitivity suggests that the gas sensitivity of the thin-film sensor is dependent on the gas sensitivity of each individual nanocrystal assuming that the thin-film sensor is composed of parallel arrangement of N number of single crystals in a vertical array. The gas sensitivity of each individual nanocrystal is determined by its surrounding reducing gas concentration, which is primarily determined by the $L(k/D_k)^{1/2}$ value. For the present microsensor, the values of k for the reactions between H_2 and CO with the surface-adsorbed oxygen species to form H_2O and CO_2 , respectively, may be assumed to be constant since the change in the free energies for similar reactions with the atmospheric oxygen is almost equivalent (-230 and -256 kJ/mol, respectively).³⁶ Hence, in the present investigation for a constant L (125–150 nm) and k values, the differences in the concentration gradients of the reducing gases (H_2 and CO) are essentially established by the differences in the corresponding D_k values. At room temperature, for a given thin-film sensor, the D_k value for H_2 is almost four times larger than that of CO, Eq. (4), which may lead to relatively flat concentration profile for H_2 than CO.³⁴ Under these circumstances, each individual nanocrystal within the thin-film sensor would have higher H_2 concentration surrounding it than that of CO. As a consequence, the H_2 sensitivity of each nanocrystal is enhanced relative to that of CO, which in turn increases the room-temperature H_2 sensitivity [according to Eq. (8)] as well as the room-temperature H_2 selectivity of the present microsensor. It is to be noted that, in the present investigation, the tetragonal- SnO_2 nanocrystallites are possibly surrounded by the hexagonal- $InSn_4$ phase, which would further modify the concentration gradient of CO within the thin-film sensor, thus, preferably increasing the room H_2 selectivity of the present microsensor over CO. Thus, the modified constitutive equation, Eq. (8), qualitatively supports the room-temperature H_2 selectivity over CO as exhibited by the present microsensor.

3. In view of surface and bulk-gas-sensing reactions and related products

The structure of the present thin-film sensor has been described schematically in Fig. 17(a). As discussed previously, the thin-film sensor has a porous binary phase structure, in which the tetragonal- SnO_2 nanocrystallites are surrounded by the hexagonal- $InSn_4$ phase. Diffuse reflectance infrared Fourier transform (DRIFT) analysis of SnO_2 powder (prepared by sol-gel) has shown that³⁷ under the ambient conditions, the surface of SnO_2 particles consists of various physisorbed and chemisorbed species involving O^- ions, coordinated H_2O , rooted and isolated OH groups, carbonate ions, and hydrated proton species (H_3O^+ and $H_5O_2^+$). The chemical reactions responsible for the formation of these surface-adsorbed species on the SnO_2 particle surface, Fig. 17(b), due to the presence of gaseous O_2 , CO_2 , and H_2O vapor in the surrounding atmosphere, are as follows:³⁷

In the present investigation, the sensor tests are conducted at room temperature with the high relative humidity (35%–50%). Since the relative humidity within the test chamber is relatively high, we assume that the sensor surface also contains OH groups along with the chemisorbed O^- ions. Under these conditions, the present microsensor responds well to the UV radiation, which is reflected in the decrease and increase in the sensor resistance in air as the UV radiation is turned on and off, respectively (Figs. 6 and 9). A gradual but very slow change in the sensor resistance with time has been observed under both conditions, which suggests the association of the oxygen-diffusion kinetics.²

FIG. 17. Schematic diagram showing the possible structure of the present thin-film sensor (a). In (b), various surface-adsorbed species present on the SnO_2 -based sensor are shown. In (c), the bulky products of CO-sensing reactions (bidentate carbonate and carboxylate) and physisorbed CO are schematically shown.

Considering the large magnitude change in the sensor resistance under the UV exposure (Figs. 6 and 9) and knowing that the thin-film sensor is porous [Fig. 4(b)], it seems that the oxygen diffusion is not only limited to the sensor-surface region but is also active within the bulk of the thin-film sensor. Hence, the presence of the chemisorbed O^- ions and OH groups has been assumed along the nanocrystallite boundaries within the entire porous thin-film sensor. This is further aided by the large surface area offered by the extremely small nanocrystallite size of 1–3 nm [Fig. 2(b)]. As a result, for achieving the maximum gas sensitivity, diffusion of the reducing gases into the thin-film sensor and their subsequent reactions with the adsorbed species are essential.

In the case of H_2 , the product of such sensing reaction is mainly H_2O [Eq. (2)], which is smaller in size relative to the size of the carboxylate (CO_2^-) and bidentate carbonate (CO_3) molecules, which are the products of CO sensing, Fig. 17(c). The chemical reactions involved in CO sensing are summarized below:³⁷

Being bulky in structure, the elimination of the intermediate and the end reaction products, involved in CO sensing, is possibly diffusion restricted at room temperature, and hence, their prolonged presence may resist the above reactions to take place within the bulk of the thin-film sensor. This may lead to only small drop in the sensor resistance in the presence of CO at room temperature [Figs. 7(b) and 10(b)]. In contrast to this, the ease of the formation and the elimination of small H_2O molecules from the mesostructured thin-film sensor results in a huge decrease in the sensor resistance in the presence of H_2 [Figs. 7(a) and 10(a)]. Thus, the differences in the concentration profiles for H_2 and CO within the thin-film sensor (due to the differences in the Knudsen diffusion coefficient) along with the differences in the product structures for H_2 - and CO-sensing reactions should strongly favor the room-temperature H_2 selectivity over CO.

4. In view of interdigitated electrode design

In the present investigation, the MEMS device with an interdigitated Au electrode configuration has been employed with the electrode distance of 20 μm . It has been recognized that^{38,39} the electrode material, the gap between the electrodes, and the electrode placement are the three critical parameters, which determine the sensitivity and the selectivity of the sensor to a particular gas. Temperature-stimulated conductance measurements suggest that³⁸ the sensitivity of the

SnO_2 -based sensors to H_2 and CO is very different depending on the electrode material (Au and Pt). The conductance of the SnO_2 -based sensors in a given atmosphere (air with H_2 or air with CO) can be obtained using the equation of the form³⁸

$$G = G_o \exp\left(\frac{-E_{act}}{kT}\right), \quad (19)$$

where E_{act} is an activation energy for the conductance in a given atmosphere. Using Eq. (19), we calculate the ratio of G_{H_2}/G_{CO} (at $T=295$ K) for Au and Pt electrodes by using the appropriate values of G_o and E_{act} for 900 ppm H_2 and CO in air, which are tabulated elsewhere.³⁷ G_{H_2}/G_{CO} for Au and Pt electrodes are calculated to be 0.133 and 57, respectively, which suggest that the sensor with Au electrode is more CO selective while that with Pt electrode is more H_2 selective. The choice of Au as an electrode material, in the present investigation, appears to be in favor of the CO selectivity.

Further, the numerical simulation results of the electrode geometry and the position effects on the semiconductor gas sensitivity suggest that³⁹ the electrodes placed at the bottom of the sensor (relative to those placed at the top) are more interesting in terms of achieving the gas selectivity. In support of this, the experimental results also suggest that⁴⁰ when the reducing gas such as H_2 tends to diffuse inside the thin-film sensor before undergoing the combustion reaction at the sensor surface, which is likely at lower operating temperatures (typically room temperature), the electrodes placed at the bottom of the sensor would give the maximum sensitivity than those placed at the top. Hence, in the present investigation, the Au electrodes placed at the bottom of the thin-film sensor would be more sensitive to the gas diffusing faster into the thin film. The flat concentration profile, as expected for H_2 , is more conducive in enhancing the room-temperature H_2 sensitivity relative to CO as the latter is likely to have a steep concentration gradient within the thin-film sensor. Hence, the bottom placement of the Au electrodes, in the present investigation, favors the H_2 selectivity over CO at room temperature.

On the other hand, the numerical simulation results have indicated that³⁹ for the bottom electrodes, the small electrode gap (within the range of 0.5–500 μm) would allow to detect poor diffusing (or reacting) gas (CO) in the presence of highly diffusing (or reacting) gas (H_2). However, with the large gap, the trend is reversed. There exists an optimum distance of 50 μm , which is insensitive to the gas concentration profile (or reactivity) and the sensor would detect both the gases with nearly same sensitivity. Since the electrode distance of 20 μm , utilized in this investigation, is very close to the optimum value, the electrode distance is less critical here in determining the gas selectivity but may slightly favor the CO selectivity.

Overall analysis shows that for the present microsensor consisting the porous, nanocrystalline, Pt-sputtered, In_2O_3 -doped SnO_2 thin-film sensor deposited on the MEMS device with bottom Au electrodes having a gap of 20 μm , the In_2O_3 doping, the mesostructure [film porosity (48%)], the small nanocrystallite size (1–3 nm), the lower operating temperature (room temperature), the small size of H_2 and

H₂O molecules, the bulky intermediate and final reaction products for CO, and the electrode placement at the bottom are the major contributing factors for the large room-temperature H₂ selectivity over CO. These factors strongly overcome the effects of other factors such as the Pt-surface catalyst, the Au electrodes, and the electrode distance of 20 μm (less critical), which may support the CO selectivity over H₂ at room temperature.

V. CONCLUSIONS

Nanocrystalline In₂O₃-doped SnO₂ thin film has been deposited on the MEMS device via sol-gel dip-coating process as a room-temperature H₂-selective sensor.

The thin-film (125–150 nm) sensor is highly porous (48%) and consists of binary phases consisting of hexagonal InSn₄ and tetragonal SnO₂. The presence of hexagonal-InSn₄ phase has been detected, but according to the authors, it possibly serves two main purposes. It avoids excessive grain growth of tetragonal-SnO₂ (sensor material) nanocrystallites (1–3 nm) after calcination at higher temperature, and secondly, since it surrounds the tetragonal-SnO₂ phase, it hinders the CO diffusion into the thin-film sensor, thus, effectively increasing the CO concentration gradient. Both of these factors favor the room-temperature H₂ selectivity over CO.

Two types of microsensors have been utilized in this report: (i) an aged sensor and (ii) the fresh sensor. The aged sensor shows one order of magnitude higher room-temperature H₂ sensitivity relative to that of the fresh sensor. It appears that the prior exposure to the UV radiation possibly sets favorable conditions for the room-temperature H₂ sensing. However, the performance of the aged sensor degraded over a period of one year as its maximum room-temperature H₂ sensitivity decreased from 10⁵ to 12 700 possibly due to the drift in its original sensor resistance in air in one year.

The present microsensor is almost insensitive to CO (900 ppm) at room temperature within the air-pressure range of 50–600 Torr. The room-temperature CO sensitivities of 1.20 and 1.02 have been recorded with and without the UV radiation, respectively.

The present microsensor is highly H₂ selective over CO at room temperature and exhibits H₂ selectivities of 317 and 12450 with and without the UV radiation, respectively. The room-temperature H₂ selectivity over CO, observed for the present SnO₂-based sensor, is much higher than some of the reported values in the higher operating temperature region (>150 °C).

In view of the various H₂ selectivity mechanisms proposed earlier, it appears that the In₂O₃ doping, the presence of hexagonal-InSn₄ phase, the small nanocrystallite size, the low operating temperature (room temperature), the meso-structure, the small size of H₂ and H₂O molecules, the bulky intermediate and final reaction products for CO, and the electrode placement at the bottom are the critical parameters, which significantly contribute to the high room-temperature H₂ selectivity of the present microsensor over CO.

The modified constitutive equation for the gas sensitivity

of the semiconductor oxide thin-film sensor, as proposed by the authors, qualitatively supports the observed room-temperature H₂ selectivity over CO based on the different concentration profiles for H₂ and CO mainly due to their differences in the Knudsen diffusion coefficients.

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