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Enhancement of H_2-sensing Properties of F-doped SnO_2 Sensor by Surface Modification with SiO_2

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Abstract: Effects of surface chemical modification with sodium silicate on the gas-sensing properties of F-doped SnO_2 gas sensor designed and fabricated employing micro-electro mechanical system (MEMS) technology were investigated. Gas sensing properties of the sensor were checked against combustible gases like H_2, CO, CH_4 and C_3H_8 at a heater voltage of 0.7 V. The H_2 sensitivity of the surface modified F-doped SnO_2 micro sensor markedly increased and reached S = 175 which was found to be about 40 times more than that of unmodified sensor (S = ~ 4.2). The increase in the sensitivity is discussed in terms of increased resistivity and reduced permeation of gaseous oxygen into the underlying sensing layer due to the surface modification of the sensor. The present micro-hydrogen sensor with enhanced sensitivity due to SiO_2 incorporation is a low energy consuming portable sensor module that can be mass-produced using MEMS technology at low cost.

Keywords: F-doped SnO_2 sensor, Surface modification, Sodium silicate, H_2 sensitivity, MEMS technology.

Introduction

The demand for a hydrogen sensor with high sensitivity, fast regeneration, and an even faster response time is gaining momentum as efforts to develop a hydrogen economy continue to grow [1-2]. Large numbers of companies and organizations such as NASA and DOE, that use large quantities of

hydrogen and oversee the development of the technology, have outlined a detailed performance criterion for an acceptable hydrogen sensor.

Tin oxide is the most used n-type semiconductor in gas sensing device because of its capabilities to detect combustible gases like CH_4, C_2H_5OH, CO, H_2 and so on [3-7]. This SnO2 based sensor is generally operated at 250°C-500°C in air. SnO_2 adsorbs oxygen from the atmosphere leading to an electron depleted zone and the reducing gases react with the adsorbed oxygen increasing thereby the electronic concentration in the material resulting in decrease of the electrical resistance. The electrical resistance of SnO_2 based sensors is controlled by a potential barrier mechanism. Due to the consumption of negatively charged oxygen adsorbates by inflammable gases, decrease in resistance is resulted because the potential barrier height decreases due to back transfer of electrons trapped by oxygen adsorbates into the outer regions of the SnO_2 particles [8-9]. Recently, room temperature operating SnO_2 based sensors were also reported. Shukla et al have reported about the hydrogen discriminating nanocrystalline doped tin oxide room temperature MEMS sensor [10] and investigated effect of air pressure, ultra violet radiation exposure as well as inverse catalytic effect at lower operating temperatures on the sensing characteristics of the sensors [11-12]. Wei et al have reported about a SnO_2 gas sensor doped with carbon nanotubes operating room temperature [13].

Previously, we have reported about synthesis of nano-crystalline F-doped SnO_2 and its application to micro gas sensor [14]. This micro gas sensor has shown higher sensitivity and better selectivity for the hydrogen gas in comparison to commercially available SnO_2. However, the sensitivity to 100ppm hydrogen gas at best heater voltage has been found to be as low as 2.8. The low sensitivity stems from the low resistivity of the F-doped SnO_2 (~ 1.8 Ω•cm). There are various techniques to modify the sensing properties of the gas sensors. One critical approach is to modify the metal oxide surface by using catalyst layer [15] or gas filter layer [16 - 18]. Wada and Egashira have reported that electrical resistance in air of SnO_2 sensors increased straightly with the amount of the incorporated SiO_2. A significant increase in sensitivity to hydrogen has also been observed with the repeated incorporation of SiO_2 on the SnO_2 surface [19].

The aim of the present study is to evaluate the effect of surface modification of F-doped SnO_2 sensor on its hydrogen sensing sensitivity. The present micro-hydrogen sensor with enhanced sensitivity due to SiO_2 incorporation is a low energy consuming portable sensor module that can be mass-produced using MEMS technology at low cost.

Materials and methods

Preparation of sample

The F-doped SnO_2 was synthesized by firing of fluoro(2-methylbutan-2-oxy)di(pentan-2,4-dionato)tin(II) at 550^{o}C for 30min. The sol-gel precursor fluoro(2-methylbutan-2-oxy)di(pentan-2,4-dionato)tin(II) was prepared by the procedure described elsewhere [20]. Figure 1 shows the surface chemical modification procedure with sodium silicate. Sodium silicate was used to incorporate SiO_2 for the surface modification of F-doped SnO_2. In the mixture solution of 0.4M boric acid and 0.4M KCl , 0.4M NaOH solution was added to attain a particular value of pH (between 9 ~ 10). To this 50 ml mixture solution, 3g F-doped SnO_2 was dispersed with constant stirring. Then 10% sodium silicate solution was added drop-wise to the buffer solution of constant pH value. The solution was further

stirred for an hour after the addition of sodium silicate. The solid sample was recovered by decantation and repeatedly washed with doubly distilled water to remove the electrolytes. Finally it was washed with methanol. The sample was dried at 60°C and then heated at 600°C for 1 hour in the furnace.

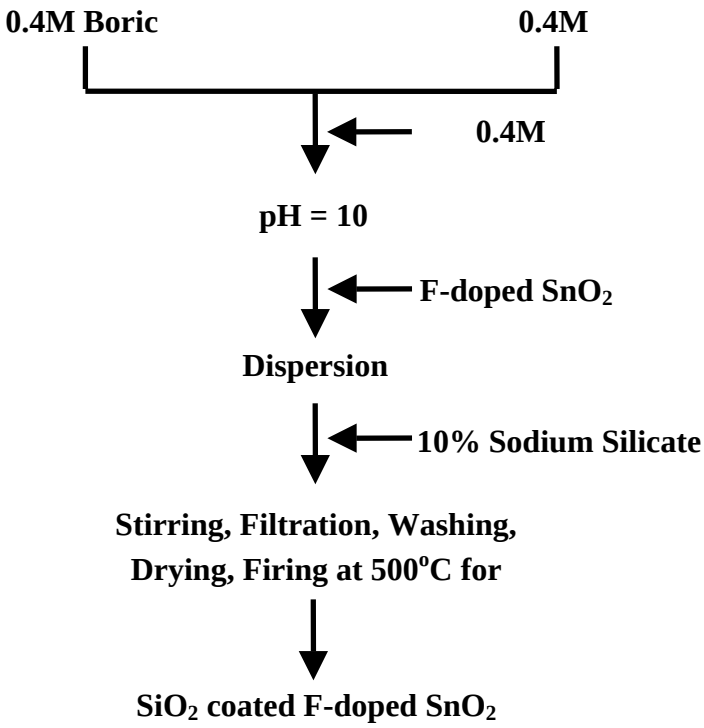


Figure 1. Schematic surface chemical modification of F-doped SnO_2 with sodium silicate.

Characterization of the modified F-doped SnO_2

The morphology of the surface modified SnO_2 was investigated by a scanning electron microscope (SEM, Philips XL-30) and an energy dispersive X-ray spectrometer (EDAX, PV99). Crystallinity and phase homogeneity of the samples were observed by powder X-ray diffraction using Philips PW 1280 diffractometer.

Fabrication of Sensor

Surface modified F-doped SnO_2 micro-sensor with SiO_2 as well as unmodified F-doped SnO_2 micro sensor was fabricated on the silicon-based substrate with Pt electrode and heater. The fabrication of the silicon-based chip is described elsewhere [14]. Nano-crystalline F-doped SnO_2 micro-sensor was fabricated on the silicon-based substrate with Pt electrode and heater. The fabrication of the silicon-based chip is made in the following steps; (a) thermal oxidation of the surface for insulating layer of SiO_2 formation, (b) pre-patterning for the cavity by wet etching with HF, (c) Cr deposition followed by Au deposition by thermal evaporation in a chamber, (d) Photo-resistive film formation by hexamethyldisilazane (HMDS) coating with spin coater (TOK, TELR N101 PM), (e) patterning for the heater and the sensing electrode (Pt electrode), (f) removing of photo-resistive film, (g) wet etching using HF for cavity making and the (h) drop coating as a micro-bead with the mixed solution of nano-

crystalline F-doped SnO_2 or surface modified F-doped SnO_2. The device was heat treated at 700°C for 6 hours in the muffle furnace and then cooled to room temperature inside the furnace. The size of the electrode was 150 µm × 80 µm with the chip area of 1.0 mm × 1.4 mm.

Temperature of sensor

Changes in heater resistance were monitored when a linearly increasing current was applied to the heaters. The resistance was converted to sensor temperature according to the well-known equation [21].

$$R_{T2} = R_{T1}[1+\alpha(T_2-T_1)]$$

Where R_{T1} is the resistance at the initial temperature, R_{T2} is the resistance at the final temperature, α is the temperature coefficient (+0.00377/^oC), T_1 is the initial temperature, T_2 is the final temperature.

Gas sensing test

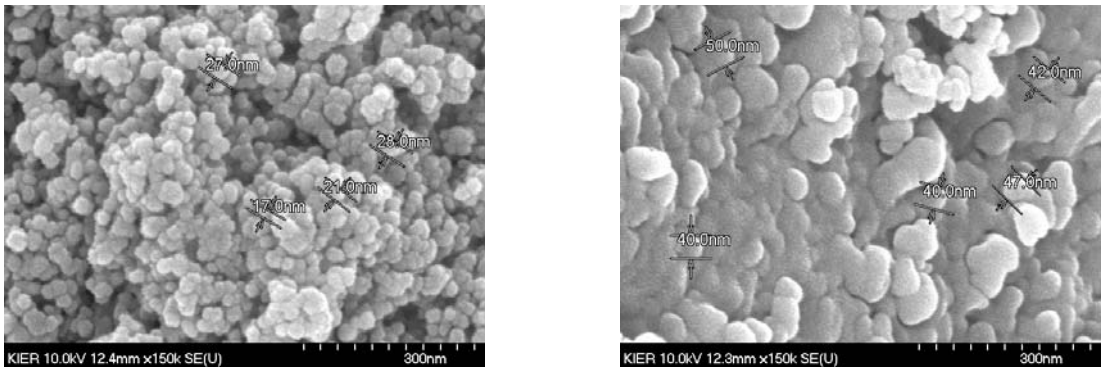
Gas sensing properties were evaluated in a gas chamber. The experimental setup for the gas sensitivity measurements was the same as those used in our previous report [14]. The sensing activity was tested by keeping the test chamber at room temperature. In the beginning, pure nitrogen gas was passed through the test chamber to remove any residual gas or water vapors then fresh air was passed and maintained till constant sensor resistance was obtained as R_a. The test gas was then admitted along with air and R_g was measured, till a constant value of R_g was obtained. Sample gases containing CO, CH_4, C_3H_8, H_2 were mixed by manual gas blender and led to the measuring chamber. (size: 250 mm × 250 mm × 160 mm). In the previous work, maximum hydrogen sensitivity of the micro-sensor was at 0.7 V [14]. Hence heater voltage of each sensor was maintained at the voltage of 0.7 V. The electrical resistances of each sensor element in air (R_a) and in a gas (R_g) were measured to evaluate gas sensitivity. Gas sensitivity was defined as the ratio ($S= R_a/R_g$) of electrical resistance of sensor in air (R_a) to electrical resistance of sensor in a particular sample gas (R_g).

Results and discussion

Microstructure of the sensor material

Figure 2 shows the SEM photographs of the F-doped SnO_2 and F-doped SnO_2 modified with SiO_2. It was observed that F-doped SnO_2 consisted of nanoparticle in the range of ~ 15 nm to ~ 30 nm, indicating an almost uniform size distribution (Figure 2a). After surface chemical treatment with sodium silicate, network slightly aggregated and particle size increased to ~ 45 nm (Figure 2b), indicating deposition of SiO_2 on the surface of F-doped SnO_2. Figure 3 shows the SEM and EDAX results of the F-doped SnO_2 modified with SiO_2**.** As shown in Figure 3a, 16.7µm x 24.3 µm area of the surface modified F-doped SnO_2 was mapped to check the presence of SiO_2 on the surface. The white points in the Figure 3b, 3c and 3d are emission lines of Sn La, F Ka and Si Ka respectively. Figure 3c

and 3d shows randomly dispersed white points. These mean uniformly doped fluorine in SnO_2 (Figure 3c) and evenly coated SiO_2 on F-doped SnO_2 (Figure 3d).



(a) (b)

Figure 2. SEM photograph of (a) F-doped SnO_2 and (b) SiO_2 coated F-doped SnO_2.

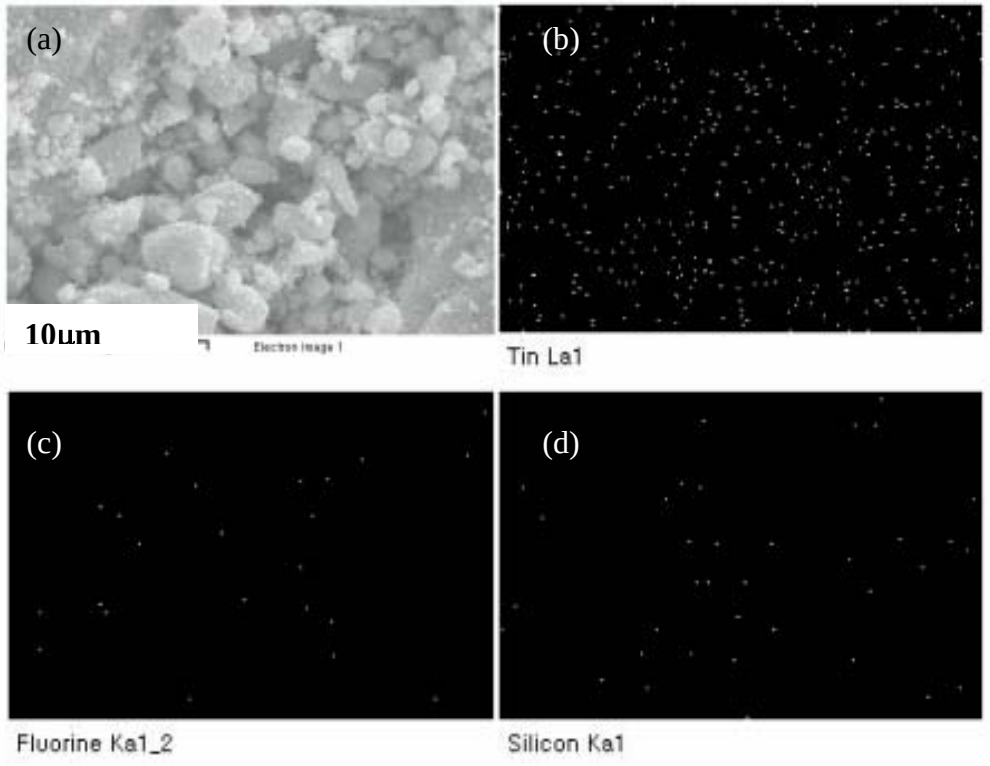


Figure 3. SEM photograph and EDAX of the SiO_2 coated F-doped SnO_2.

Surface modified F-doped SnO_2 as well as unmodified F-doped SnO_2 were also characterized by XRD technique (Figure 4). The F-doped SnO_2 had a cassiterite structure without any impurity (JCPDS 41-1445). The nanocrystalline nature of the F-doped SnO_2 and F-doped SnO_2 modified with SiO_2 was confirmed by the broad peaks in the XRD pattern. Decreased intensity of the surface modified F-doped SnO_2 can be explained by the scattering of the X-ray by SiO_2 thin layer on F-doped SnO_2.

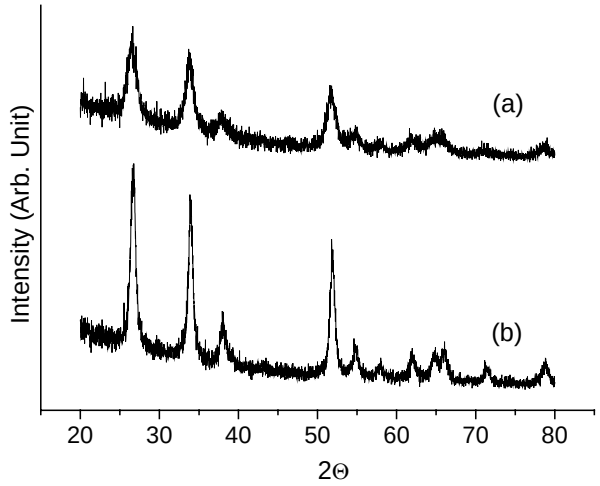


Figure 4. X-ray diffraction pattern of (a) SiO_2 coated F-doped SnO_2 (b) F-doped SnO_2.

Gas sensing property

Hydrogen has a much wider range of flammability in air 4% to 75% by volume and the lowest limit of hydrogen concentration in air to explosion is 4.65% [22]. These characteristics would tend to indicate that flammability is a greater risk for hydrogen than for other fuels. In many accidental situations the lower flammable limit (LFL) is more important. The LFL for hydrogen is similar to that of methane, about twice that of propane, and four times that of gasoline. So, the development of a sensor with high performance should be to detect from ppm level to a few percentage of the gas in air. In this investigation, the detection of low concentration of hydrogen (ppm level) was kept as a target. Concentrations ranging from 100 to 600 ppm of H_2, CH_4, C_3H_8, and CO were injected in the test chamber and the sensing signals were recorded. The sensor was operated at 0.7 V. This heater voltage was selected because the selectivity and sensitivity for the hydrogen was the best at this voltage [14]. The calculated heater temperature at this voltage was 320 ^oC as shown in Figure 5.

Sensitivities of the micro-sensor made with nano-crystalline F-doped SnO_2 as well as with SiO_2 modified F-doped SnO_2 against various reducing gases were recorded. As shown in the Figure 6a, the surface modified F-doped SnO_2 showed very high sensitivity for H_2, on introduction of 600ppm hydrogen gas (S = 175). On the other hand, the sensitivities to C_3H_8, CO, and CH_4 were relatively low(S = 1-3), as seen in Figure 6a. It is obvious that incorporation of SiO_2 is very much effective for the enhancement of the sensitivity of sensor to the hydrogen. But the sensitivity to C_3H_8, CO, and CH_4 increased slightly. This may be due to the difference in molecular size between H_2 and these gases. Small H_2 molecules can go through the aggregated SiO_2 particles to react with negatively charged oxygen adsorbates on the surface of the sensor, while large C_3H_8, CO, and CH_4 molecules are prevented from reaching the surface of F-doped SnO_2 by SiO_2 particles. Similar behavior in the gas-sensing properties of the sensor after surface modification was observed and explained on the basis of difference in molecular size and decreased oxidation activities by Wada and Egashira [19].

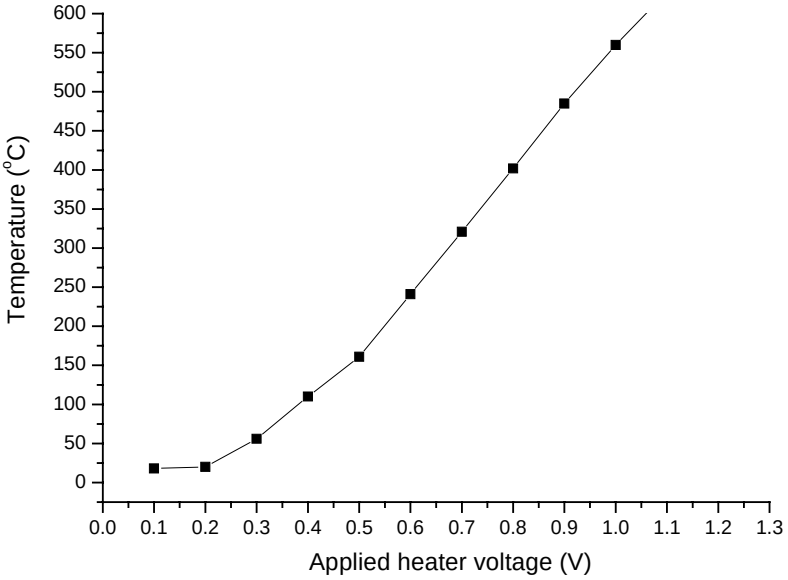


Figure 5. Heater temperature vs. applied heater voltage.

Comparison of the sensors made with surface modified F-doped SnO_2 and unmodified F-doped SnO_2

F-doped SnO_2 has shown higher sensitivity to hydrogen gas in comparison to the commercially available SnO_2 sensor [14]. The higher sensitivity and selectivity of the nano-crystalline F-doped SnO_2 for hydrogen gas may be due to the greater adsorption of hydrogen molecules on the favorable sites at fluorine atoms of the materials or the increased n-type property of SnO_2 by fluorine doping. Higher sensitivity shown by nano-crystalline F-doped SnO_2 is also because of its higher surface area. Similar results have been obtained on SnO_2 nano-crystalline H_2 gas sensors for their sensitivities by Seal and Shukla [23] and Gong et al. [24]. However, the sensitivity to 600ppm hydrogen gas at best heater voltage was ~ 4.2 (Figure 6b). The H_2 sensitivity of the surface modified F-doped SnO_2 micro sensor markedly increased and reached S = 175 on introduction of 600ppm hydrogen (Figure 6a). Although the sensitivity of the present device to hydrogen is not very high but still the value of sensitivity of this surface modified F-doped SnO_2 sensor to hydrogen, is about 40 times more than that of unmodified sensor. This might be explained by the increased resistivity of the F-doped SnO_2 due to the surface modification with SiO_2. It has been observed in our previous report that F-doped SnO_2 had good selectivity to H_2 but its sensitivity was low because of the reduced resistivity [14]. Wada and Egashira have reported that electrical resistance of the SnO_2 sensor in air increased straightly with the amount of the incorporated SiO_2 resulting in the increase of H_2 sensitivity [19]. So, in this case also, incorporated SiO_2 on the surface of F-doped SnO_2 is responsible for increase in electrical resistance of the sensor, resulting in the remarkable increase of its sensitivity to hydrogen. As SiO_2 particles can reduce permeation of gaseous oxygen into the underlying sensing layer and hence to enhance the gas sensitivity due to the suppressed oxygen readsorption. Also, it was found that the hydrogen oxidation activity of SnO_2 was promoted by the incorporation of the SiO_2 component [18]. Anyway, it should be noted that the surface chemical modification with SiO_2 resulted in a remarkable increase in the

hydrogen sensitivity of the sensor. The present micro-hydrogen sensor with enhanced sensitivity due to SiO_2 incorporation is a low energy consuming portable sensor module that can be mass-produced using MEMS technology at low cost.

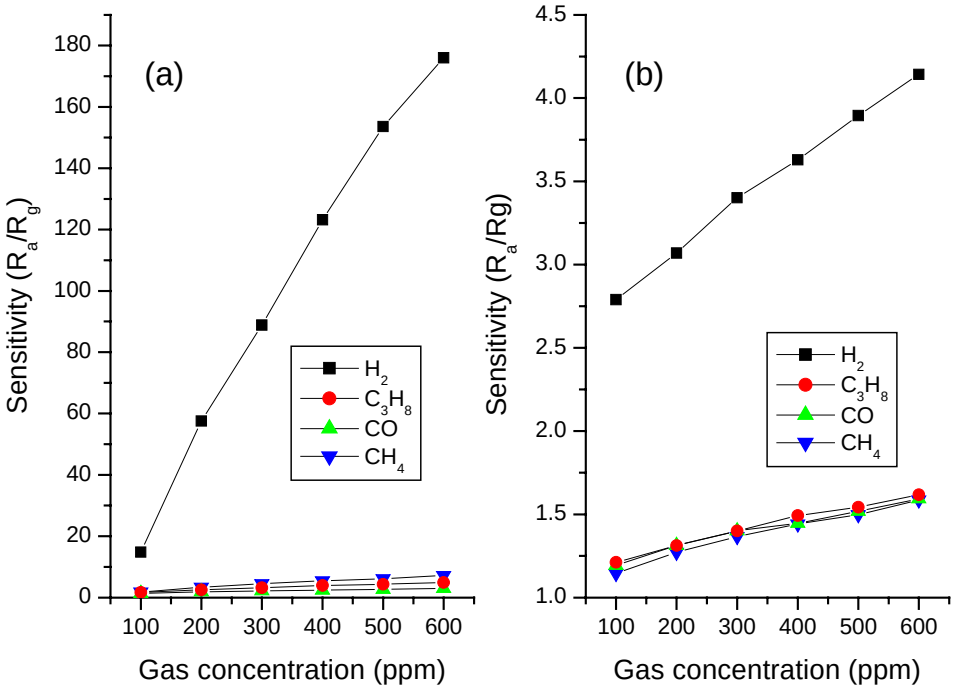


Figure 6. Sensitivity as a function of gas concentration of the (a) SiO_2 coated F-doped SnO_2 sensor and (b) F-doped SnO_2 sensor, at heater voltage of 0.7 V.

Response and recovery times of the sensor

Response and recovery times are the important parameters of gas sensor. The time taken for the sensor to attain 80% of the maximum change in resistance upon exposure to the gas is the response time. The time taken by the sensor to get back 80% to the original resistance is the recovery time. Figure 7 shows variation in logarithmic resistance of the SiO_2 coated F-doped SnO_2 sensor upon exposure to and removal of 600ppm H_2 at 320^{o}C. The response time calculated for the sensor was T_{80}=58sec. In contrast, the recovery time was very slow and prolonged at 320^{o}C as seen in Figure 7. Similar behavior of response and recovery time of the surface modified SnO_2 sensors with SiO_2 has been reported by Wada and Egashira [19].

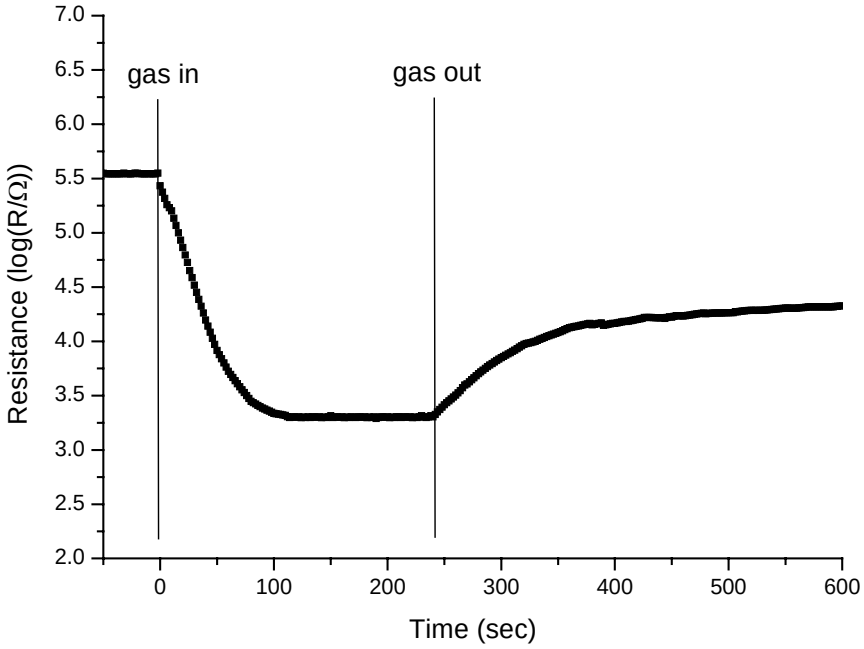


Figure 7. Transient response curves to 600ppm H2 at 320oC of the SiO2 coated F-doped SnO2 sensor.

Conclusions

Hydrogen sensitivity of F-doped SnO_2 sensor could be improved by surface chemical modification with sodium silicate treatment. SEM and EDAX observations revealed the existence of fine SiO_2 particles on the surface of the sensor. The maximum hydrogen sensitivity of the sensor was at a heater voltage of 0.7 V. The H_2 sensitivity of the surface modified F-doped SnO_2 micro sensor markedly increased and reached S = 175 which was found to be about 40 times more than that of unmodified sensor (S = ~ 4.2). The increase in the sensitivity is discussed in terms of increased resistivity and reduced permeation of gaseous oxygen into the underlying sensing layer due to the surface modification of the F-doped SnO_2 with SiO_2. The present micro-hydrogen sensor with enhanced sensitivity due to SiO_2 incorporation is a low energy consuming portable sensor module that can be mass-produced using MEMS technology at low cost.

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