Research Article

Size-Selected $\text{SnO}_{1.8}$: Ag Mixed Nanoparticle Films for Ethanol, CO, and CH_4 Detection

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Mixed nanoparticle films of $\text{SnO}_{1.8}$: Ag prepared by the gas phase condensation method using an aerosol route have been used for the detection of CO and CH_4 . Particle size as estimated by transmission electron microscopy is 20 nm for both $\text{SnO}_{1.8}$ and Ag nanoparticles. The gas-sensing behavior of the films for these gases has been studied in detail as a function of Ag concentration in the films. A study has been made in order to distinguish the size effect and specific surface area effect in the ethanol gas-sensing behavior of $\text{SnO}_{1.8}$: Ag mixed nanoparticle films. This distinction, which has not been possible using the traditional methods of the sensor fabrication, gives evidence of the dominance of size effect of the metal dopant over the surface area effect in the gas sensing of the films. The sensors show also an increased sensor signal with increase of Ag concentration in the films for CO and CH_4 . It is observed from the comparative study of the sensing behavior of $\text{SnO}_{1.8}$: Ag films for CO and CH_4 that the sensors are more sensitive towards CO as compared to CH_4 . The mixed nanoparticle films were also used for the detection of CO at 100 ppm level.

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1. INTRODUCTION

Several methods have been used to prepare metal oxides with high surface area for conductive gas sensor applications. Conductive sensors change their conductivity when reacting with the oxidizing or reducing gases. Among the variable conductivity sensors, the metal oxides are one of the most popular technological choices. Main advantages of metal oxide sensors are a high sensitivity, long-term stability, and the possibility of integration. It is known that the gas-sensing characteristics of a metal oxide semiconductor can be improved by the introduction of metal particles on the host semiconductor material [1–4]. The interest of combining the noble metal nanoparticles with semiconductor oxides basically relies on the metal ability in acting both as sink for electrons or as redox catalyst. For this purpose, many noble metals have been introduced to the SnO_x , a most used metal oxide for gas sensors, in order to enhance the gas-sensing characteristics. The effect of metal introduction on gas-sensing properties of tin oxide has been studied in detail using metals like Pt, Pd, Au, and Ag. Amongst them Pt [2, 3] and Pd

[1] are the most used metal nanoparticles whereas Ag [5–7] have also been reported to act as catalytic particles for the gas sensing by SnO_x . We have studied the ethanol-sensing characteristics for Ag- SnO_x mixed nanoparticles in our earlier report [8–11]. The present article also reports the applicability of size selected $\text{SnO}_{1.8}$: Ag nanoparticles to detect CO and CH_4 gases.

In the traditional preparation techniques, it is not possible to separate the metal particle size effect and surface area effect in the metal-based metal oxides. Using a well-defined aerosol route, we made an attempt to understand the effect of the variation in metal particle size on the gas sensing of monodisperse $\text{SnO}_{1.8}$: Ag nanoparticle films with the variation of Ag concentration. From this study it is expected to clarify the distinction between size effect and surface area effect for the gas sensors. The distinct advantages of aerosol route over alternative methods is a very high level of control over grain size and doping level by generating both SnO_x nanoparticles as well as dopant (Ag) nanoparticles separately, selecting the desired particle sizes and then mixing them homogeneously as aerosols according to the required

Ag content in SnO_x films. Furthermore, an in-flight sintering at high temperature stabilizes the SnO_x against grain growth in the film, thereby increasing its long-term stability. The Ag particles are added to the films at the concentrations of 0.1, 1.0, and 5%, based on number concentration.

In this work, we have studied in detail the effect of Ag concentration on ethanol-sensing properties of the $\text{SnO}_{1.8}$: Ag nanoparticles prepared by aerosol route. We focus on developing a methodology in order to discriminate between size and surface effects, as we are able to vary independently the particle size and concentration. This is performed for ethanol detection. Furthermore, the detection of CO and CH_4 is shown to be feasible.

2. EXPERIMENTAL

A well-defined gas-phase synthesis method has been used for the preparation of crystalline monodisperse $\text{SnO}_{1.8}$: Ag particles [8, 9]. SnO and Ag are used as source for nanoparticles in two different furnaces. Radioactive β -source (Kr^{85}) acting as bipolar aerosol chargers were used along with differential mobility analyzers (DMA) for size classification for SnO and Ag aggregates. In the second half of the sintering/crystallization furnace (operated at 650°C) a flow of O_2 is added in order to oxidize the SnO nanoparticles to SnO_x nanoparticles, with $x > 1$. Ag is added to the films in the form of nonsintered Ag nanoparticles at the concentration level 0.1 to 5%, based on particle concentration.

In order to deposit nanoparticle films, a precipitator was used which can act either as low-pressure impactor (LPI) or as electrostatic precipitator (ESP). The LPI has been used here for depositing $\text{SnO}_{1.8}$: Ag nanoparticle films for gas-sensing application. The method of preparation for the size-selected $\text{SnO}_{1.8}$: Ag nanoparticles for $[\text{Ag}] = 0.1, 1\%, \text{ and } 5\%$ is discussed elsewhere [8]. It is seen that the particle size for $\text{SnO}_{1.8}$ and Ag nanoparticles estimated using transmission electron microscopy was identical to the value selected by the DMA. Resistance measurements of the nanoparticle films in different gas environment were carried out by using an automated setup including a picoammeter with an internal voltage source. Details of the gas-sensing measurement setup with definitions for sensor signal, response time, and recovery times are described in previous report [8, 9, 12].

3. RESULTS AND DISCUSSION

Transmission electron microscopy (TEM) has been used for particle size determination of the $\text{SnO}_{1.8}$ and Ag nanoparticles. Figure 1 shows TEM micrographs for $\text{SnO}_{1.8}$ (Figure 1(a)) and Ag (Figure 1(b)) nanoparticles. The particle size for both $\text{SnO}_{1.8}$ and Ag nanoparticles is 20 nm. The gas-sensing properties of $\text{SnO}_{1.8}$: Ag nanoparticle films are discussed. The gases to be tested are ethanol, CO, and CH_4 , these are reducing gases. The deposition conditions were chosen such that the estimated thickness ($\sim 1.5 \mu\text{m}$) of $\text{SnO}_{1.8}$: Ag films and particle size of 20 nm for $\text{SnO}_{1.8}$ and Ag remains the same, but the Ag concentration can be varied.

(a)

(b)

FIGURE 1: TEM micrographs for $\text{SnO}_{1.8}$ nanoparticles (a) and Ag nanoparticles (b).

The mixed $\text{SnO}_{1.8}$: Ag nanoparticle films were tested for their sensing behavior towards ethanol vapor to measure the sensor signal and response time. The sensor signal is defined as the ratio of resistance in air to resistance in ethanol gas (R_a/R_g) and response time is the time needed for the conductance of the gas sensor to obtain 90% of the maximum conductance when ethanol gas is introduced into an environment of synthetic air. We have reported an increase in the value of sensor signal and decrease in response time with an increase of Ag content in the mixed films [8, 10] for ethanol. We will now, however, concentrate on distinguishing the size effect and specific surface area effect in the ethanol gas-sensing behavior of $\text{SnO}_{1.8}$: Ag mixed nanoparticle films.

As in $\text{SnO}_{1.8}$: Ag mixed nanoparticle films, both changes in particle size as well as in the concentration will change the total surface area of the catalyst particles, we define the specific surface area (SSA) of the Ag nanoparticles, based on the total mass of the $\text{SnO}_{1.8}$ plus Ag mixture. The specific surface area values can be calculated by

$$\text{SSA (Ag in mixture)} = \frac{s_{\text{Ag}}}{(\rho_{\text{Ag}} V_{\text{Ag}} + \rho_{\text{SnO}_{1.8}} V_{\text{SnO}_{1.8}} (N_{\text{SnO}_{1.8}}/N_{\text{Ag}}))} \quad (1)$$

with s_{Ag} as the surface area of the Ag nanoparticles in m^2 and ρ , V , and N are as the density, total volume, and number of the nanoparticles of $\text{SnO}_{1.8}$ and Ag. The values of the SSA are

FIGURE 2: (a) Dependence of specific surface area on particle size of Ag nanoparticles for $\text{SnO}_{1.8}$: Ag sensors and (b) variation of sensor signal for detection of ethanol with specific surface area for $\text{SnO}_{1.8}$: Ag sensors (at 400°C for 1000 ppm ethanol).

plotted against the size of Ag nanoparticles in Figure 2(a). Figure 2(b) shows the variation of sensor signal with specific surface area. Here we observe an important result which is, the gas-sensor signal for ethanol increases with an increase of SSA for the mixture and decrease of Ag particle size in the mixed films. Note that on increasing the size of Ag nanoparticles the SSA increases whereas the gas-sensor signal for 1000 ppm ethanol decreases. The SSA in our mixed films is increasing due to the increase of Ag concentration in the films. Therefore, the increase of sensor signal with Ag concentration is due to the increase of available SSA whereas

FIGURE 3: Variation of response time for 1000 ppm ethanol with specific surface area for $\text{SnO}_{1.8}$: Ag sensors (a) and variation of recovery time in synthetic air with specific surface area for $\text{SnO}_{1.8}$: Ag sensors (b).

the increase in sensor signal with reduction of particle size is a size effect rather than a surface area effect. This shows the clear evidence of the dominant nature of size effect of the metal dopant over the surface area effect on the gas-sensing behavior for the films.

The dependence of response and recovery time on the size of Ag particles and SSA of the catalyst are shown in Figures 3(a) and 3(b). The response and recovery times for the sensors with $[\text{Ag}] = 5\%$ decrease from 5 seconds to 2 seconds, and 160 seconds to 46 seconds, respectively, on decreasing the Ag particle size from 20 to 5 nm in the mixed

(a)

(b)

FIGURE 4: Variation of (a) sensor signal ($\text{SnO}_{1.8}$: Ag, 20 nm, 1.5 μm , $T = 400^\circ\text{C}$) and (b) response time ($\text{SnO}_{1.8}$: Ag (5%), 20 nm, 1.5 μm , $T = 400^\circ\text{C}$) for CO and CH_4 with Ag concentration for $\text{SnO}_{1.8}$: Ag nanoparticle films.

films. In the case of $[\text{Ag}] = 1\%$, response time decreases from 15 to 10 seconds and recovery time changes from 175 to 105 seconds and for $[\text{Ag}] = 0.1\%$ response and recovery times decrease from 20 to 15 seconds and 200 to 160 seconds, respectively, on decreasing the size of Ag nanoparticles from 20 nm to 10 nm in the mixed films. The stronger dependence of the response and recovery times on the Ag particle size as compared to SSA of the catalyst can be seen from the plots.

The SnO_2 -based sensors vary their conductivity in presence of oxidizing and reducing gases, because the absorption and desorption of O^- , O_2^- , and O^{2-} at the sensor surface changes the electron density at the semiconductor surface.

(a)

(b)

FIGURE 5: Sensor signal for $\text{SnO}_{1.8}$: Ag mixed nanoparticle films on repeatedly switching from synthetic air to (a) 1000 ppm CO ($\text{SnO}_{1.8}$: Ag (5%), 20 nm, 1.5 μm , $T = 400^\circ\text{C}$) and (b) 1000 ppm CH_4 ($\text{SnO}_{1.8}$: Ag (5%), 20 nm, 1.5 μm , $T = 400^\circ\text{C}$).

The adsorbed oxygen gives rise to potential barriers at grain boundaries and thus increases the resistance of the sensor surface, on the other hand reducing gases decrease the oxygen surface concentration and hence the sensor resistance. The magnitude of the response depends on the nature and concentration of the volatile molecules, and also on the type of metal oxide. An increase in the value of sensor signal and decrease in response time with increase of Ag concentration (up to 5%) for the $\text{SnO}_{1.8}$: Ag mixed films has also been observed for methane and carbon monoxide. Figures 4(a) and 4(b) show the variation of sensor signal and response time with Ag concentration in the films. It is seen that the sensors are more sensitive toward CO in comparison of CH_4 . It is interesting to note that the sensing response of the sensors is faster for CH_4 than for CO. The sensors are observed to be reproducible. Figure 5 shows the variation of sensor signal with time for $\text{SnO}_{1.8}$: Ag [5%] sensors for 1000 ppm

FIGURE 6: Sensor signal for $\text{SnO}_{1.8}:\text{Ag}$ mixed nanoparticle films on repeatedly switching from synthetic air to 100 ppm CO ($\text{SnO}_{1.8}:\text{Ag}$ (5%), 20 nm, $1.5\ \mu\text{m}$, $T = 400^\circ\text{C}$).

CO or CH_4 . These sensors are observed to be also suitable for the CO and CH_4 based on the value of sensor signal and response time. The difference in the sensor signals for the different gaseous environment are expected to be useful for the development of gas discriminating sensors, for example, on the basis of principal component analysis or neural networks.

$\text{SnO}_{1.8}:\text{Ag}$ nanoparticle gas sensors were also tested for their potential applicability in detection of lower concentration. Response plots for $\text{SnO}_{1.8}:\text{Ag}$ [5%] in 100 ppm CO are shown in Figure 6. The response time measurements on $\text{SnO}_{1.8}:\text{Ag}$ films show a response time of 8 minutes 100 ppm CO for $[\text{Ag}] = 5\%$ sensor. It can be expected that, similar to the ethanol detection, the use of smaller Ag nanoparticles will greatly reduce this response time.

4. CONCLUSIONS

Ag particle size dependence on the gas-sensing behavior of $\text{SnO}_{1.8}:\text{Ag}$ mixed films have been studied using tailored nanoparticle films. The sensors were found to be strongly dependent on the Ag particle size. Sensors with optimized Ag concentration of 5%, and Ag particle size of 5 nm have successfully been used to detect ethanol. The gas sensor is shown to yield a different behavior in the case of exposition to CO and CH_4 . The present study is expected to be useful for developing advanced sensing materials for ppb-level gas detection, as well as gas discrimination device.

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