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# Gas Sensing Properties of $Co_3O_4$-loaded $SnO_2$ to Ethanol and Acetone

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A series of $Co_3O_4$-loaded $SnO_2$ nanocomposite thick films were prepared by grinding, screen-printing and sintering at 700 °C for 3 h. XRD data showed the nanocomposite thick films were rutile structure of $SnO_2$ and cubic $Co_3O_4$. The composite films were found to exhibit good response to alcohol and acetone at 300 °C. The film went through a sharp sensitivity maximum at 5 mol%$CoO_{4/3}$ with a change in $Co_3O_4$ content. At 300 °C, the maximum sensor response to alcohol and acetone, each 1000 ppm in air, was 301 and 235, respectively, which was about 7 and 5 times as large as that of the pure $SnO_2$ respectively. The selectivity to alcohol and acetone over $H_2$ and CO also was promoted by the addition of $Co_3O_4$ to $SnO_2$. The mechanism of such strong promotion of sensor response (electronic sensitization) is discussed.

**Key words:** Tin oxide, Cobalt oxide, Gas sensor, Electronic sensitization, Acetone, Alcohol

## I. INTRODUCTION

As industry is developing, numerous kinds of gases are emitted from various sources into our living space. Most of them are hazardous to human health, such as industrial emissions or leaked gas, while some others such as ethanol and acetone in the breath and flavor components of foods, which can be used to diagnose the state of their sources, are useful. Most of these useful gases are present at very low concentrations, so gas sensors with extremely good sensing property are required for their monitoring. Resistive-type gas sensors using semiconducting metal oxides have been put into practice for many years for a variety of applications because of low cost, high sensitivity, fast response speed and low power consumption [1-4].

Gas detection of resistive-type gas sensors is achieved by the change of conductivity in air and in reducing or oxidizing gas atmospheres. It is generally accepted that these materials change their conductivity in the presence of oxidizing and reducing gases as electron density at the surface gets modified due to absorption and desorption of $O^-$, $O_2^-$ or $O^{2-}$. This adsorbed oxygen gets trapped at the grain boundary trap states and thereby increases the grain boundary potential barrier. This results in a decrease in the conductivity of the material. For reducing gases, the trap states get depleted of charged carriers and thereby reduce the resistance through lowering of the potential barrier at the grain boundaries [8]. Among the semiconducting metal oxides used for resistive-type gas sensors, tin oxide is the most widely used semiconducting metal oxide for its selective electrical conductance, high thermal and chemical stability. The tin oxide sensor material is sensitive to almost all the gases, both reducers and oxidants [5-7], though the response is different for each gas. However, for detecting these gases at very low concentrations, further enhancement of gas sensing properties of this type is still in great demand.

Many approaches have been made to achieve high sensitivity and selectivity, such as lowering of operating temperature, irradiation, incorporation of specific additives, controlling the sensor operating temperature, and use of masks and filters [9-12]. The incorporation of a second component in metal oxides as bulk doping or surface modification is one of the most attractive methods for the enhancement of gas sensing properties. Various noble metal oxides, such as $Ag_2O$ [13], PdO [14,15], have been widely used as additives. When these additives are dispersed on the grain surface, they can act as foreign receptors for the target gas species, leading to a great enhancement of gas sensitivity of the device. However, the noble metals are expensive.

$Co_3O_4$, a p-type semiconductor, has been recently proposed as a new sensitive material for resistive-type gas sensors because of its low cost compared to noble metals. $Co_3O_4$ was first tested as a promoter for $In_2O_3$-based CO sensors [16]. Recently, $Co_3O_4$ has been used as a promoter for $SnO_2$-based CO and $H_2$ sensors at a relative lower temperature [17,18], but the selectivity to other gases and the mechanism need further study. In this work, a series of $Co_3O_4$-loaded $SnO_2$ composites with 0-10 mol%$CoO_{4/3}$, prepared by mechanical mixing and calcinations, were tested for sensing properties to alcohol and acetone. The response to alcohol and acetone was greatly enhanced at 5 mol%$CoO_{4/3}$. We reports the sensing properties and the mechanism of $Co_3O_4$-loaded $SnO_2$ composites to alcohol and acetone.

## II. EXPERIMENTS

Nano-powders of $SnO_2$ and $Co_3O_4$ were prepared from reagent $SnCl_4 \cdot 5H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, respec-

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tively. Each starting chemical together with deionized water was stirred under constant agitation and the pH of the suspension was adjusted to 7 by dropwise addition of diluted ammonia solution. The precipitates were collected by filtration, and washed with deionized water. After drying at 80 °C for several hours, the precipitates were ground in an agate mortar and calcined at 600 °C for 2 h. The nano powders of $SnO_2$ and $Co_3O_4$ were mixed to designated compositions and each mixture was grounded in an agate mortar for half an hour. The mol% of Co/Sn varied between 0 and 10%.

The powder phases were characterized by X-Ray diffraction (XRD) (Philips X'pert PRO SUPER) and the crystallite size of powders were calculated according to Scherrer's equation. X-ray photoelectron spectroscopic (XPS) (ESCALABMKII) studies were carried out on pure and $Co_3O_4$-loaded $SnO_2$ to establish the sensing mechanism of these materials.

By using a binary dispersant of $\alpha$-terpineol (95%, mass)-ethyl cellulose (5%, mass), each composite powder was converted into a paste. $Co_3O_4$-loaded $SnO_2$ composites used as sensitive body were fabricated on alumina tubes with Au electrodes and platinum wires. A Ni-C alloy crossing alumina tube was used as a resistor. This resistor ensured both substrate heating and temperature control. Each element was sintered at 700 °C for 3 h in air. The gas sensors were aged in air for 10 days to improve their stability and repeatability. The gas response of the sensors was studied in a sealed test chamber (5 L) with an inlet and an outlet. The test gas was injected into the test chamber through the inlet port and the resistance was measured as a function of time till a constant value was attained. The gas sensitivity (S) is defined as $R_a/R_g$, where $R_a$ and $R_g$ are the electric resistance in air and the sample gas, respectively [19].

## III. RESULTS AND DISCUSSION

### A. $Co_3O_4$-loaded $SnO_2$ composite powders

XRD patterns of the $Co_3O_4$-loaded $SnO_2$ composite powder, calcined at 700 °C for 3 h, are shown in Fig.1. All diffraction lines are ascribed to rutile structure of $SnO_2(\triangle)$ or cubic $Co_3O_4(\square)$, confirming the absence of any reaction products in between. From Sherrer's equation, XRD results indicate that the content of $Co_3O_4$ has no significant effect on crystallite size (D).

### B. Sensor response of $Co_3O_4$-loaded $SnO_2$ composite films

Thick films of $Co_3O_4$-loaded $SnO_2$ composites were measured for electrical resistance in air ($R_a$). Figure 2 shows the resulting data at 300 °C as a function of $Co_3O_4$ content. With increasing Co content from 0 to
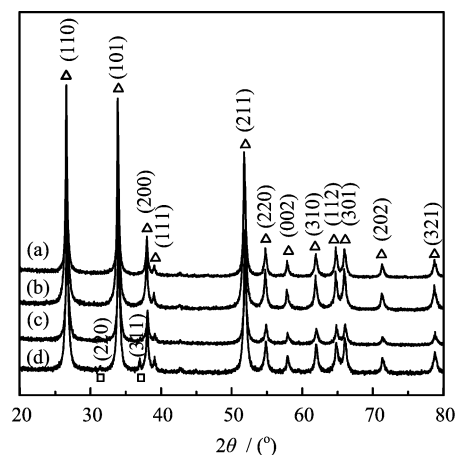
FIG. 1 XRD patterns of $CoO_{4/3}$-loaded $SnO_2$. $\triangle$ $SnO_2$, $\square$ $Co_3O_4$. (a) Pure $SnO_2$. (b) 2 mol%Co-loaded $SnO_2$. (c) 5 mol%Co-loaded $SnO_2$. (d) 10 mol%Co-loaded $SnO_2$.

5 mol%, $R_a$ is seen to increase sharply by about two orders of magnitude (from $10^5$ $\Omega$ to $10^7$ $\Omega$). Such a sharp increase in $R_a$ with increasing amount of additives has been reported for $SnO_2$-based sensors loaded with $Ag_2O$ [13] and PdO [14,15]. $R_a$ does not seem to increase any more with further Co content increasing.
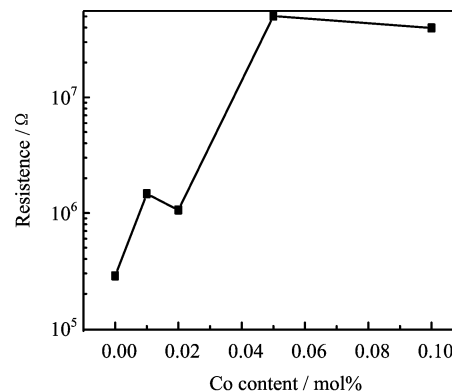
FIG. 2 Electrical resistances in air at 300 °C as a function of $CoO_{4/3}$ content.

Though $Co_3O_4$ is a p-type conductor, $Co_3O_4$-loaded $SnO_2$ (in our mole ratio) still shows n-type response to reducing gases (the electrical resistance decreases on exposure to reducing gas) in air at 300 °C. $SnO_2$ is a typical n-type conductor, so perhaps the small mole rate of $Co_3O_4$ does not change it to a p-type. Figure 3 shows the gas sensitivity of two composites to 1000 ppm alcohol as a function of operating temperature. The gas sensitivity exhibits a volcano-shaped relation with the operating temperature, reaching a maximum at 300 °C in each case. The addition of $Co_3O_4$ does not result in a shift of the volcano-shaped correlations between gas response and temperature toward the lower temperature side. This is different from $Ag_2O$- and PdO-loaded

SnO$_2$ sensors which make the best operating temperature shift toward the lower temperature side [13-15]. Nevertheless, it was found that the sensitivity to alcohol at 200 °C is also large enough for application as low energy consumption.
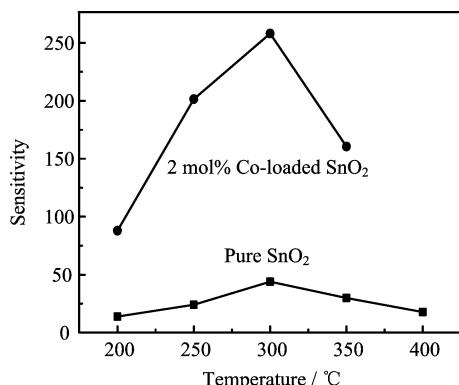


FIG. 3 Sensitivity of the sensors to alcohol as a function of temperature.

The sensor response to alcohol and acetone (1000 ppm) at 300 °C is plotted as a function of Co$_3$O$_4$ content in Fig.4. The sensor response depends very sensitively on Co$_3$O$_4$ content, going through a sharp maximum at 5 mol%. The largest response to alcohol and to acetone (301 and 200) attained at 5 mol%Co is 7 and 5 times as large as that of the pure SnO$_2$ (42 and 40) respectively. The response of 5 mol%Co to alcohol and acetone is far larger than that of pure SnO$_2$, proving a very marked promoting effect of Co$_3$O$_4$ loading. The sensor response of pure Co$_3$O$_4$ to several gases (1000 ppm) at 300 °C is also plotted in Fig.4. It is quite small compared to the sensor response of pure SnO$_2$, so the promoting effect of Co$_3$O$_4$ loading is not caused by the sensor response of Co$_3$O$_4$ itself. The sensor response degrades when excessive Co$_3$O$_4$ is added. Perhaps too many reactive sites make it more difficult for reducing gas molecules to diffuse into the inner part of thick
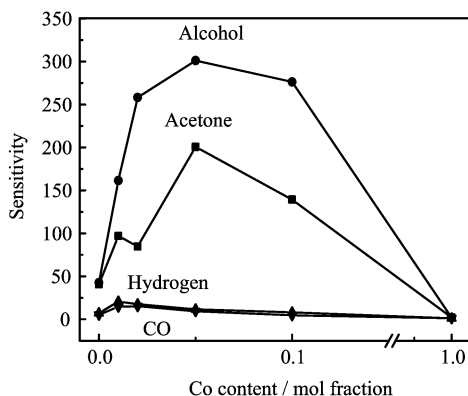
films, as illustrated by the reaction-diffusion equation-based analysis of gas sensing properties [17].

The sensor response to H$_2$ and CO (1000 ppm) is also plotted as a function of Co$_3$O$_4$ content in Fig.4. The response to H$_2$ and CO (300 °C) has no significant change as Co$_3$O$_4$ content increases. Thus, the response ratio ($S_{alcohol}/S_{hydrogen/CO}$ or $S_{acetone}/S_{hydrogen/CO}$), also called selectivity, is promoted substantially by this change. Figure 5 shows the time dependence of sensitivity of pure and 5 mol%CoO$_{4/3}$-loaded SnO$_2$ exposed in 1000 ppm alcohol, acetone and air. It was found that response time (less than 1 min) and recovery time (several seconds) are short enough for application. Sn3d$_{5/2}$ (ground state) XPS spectra of pure and CoO$_{4/3}$-loaded SnO$_2$ has been obtained by XPS as showed in Fig.6. It was found that the XPS binding energies (BE) of the inner orbits of Sn, typically Sn3d$_{5/2}$, shift downward. The shifts are as large as 0.15 eV. There are also similar reports on XPS studies on PdO and Ag$_2$O in SnO$_2$ [13,14].
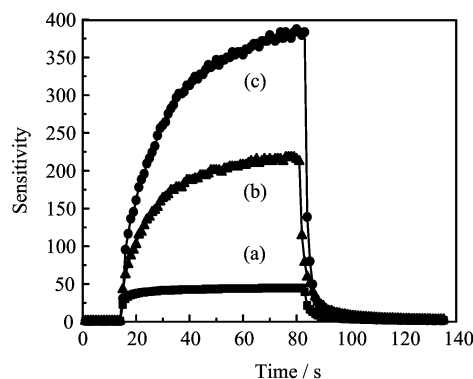


FIG. 5 Response transients to 1000 ppm alcohol of pure SnO$_2$ and 5%CoO$_{4/3}$-loaded SnO$_2$. (a) Pure SnO$_2$ (alcohol). (b) 5 mol%Co-loaded SnO$_2$ (alcohol). (c) 5 mol%Co-loaded SnO$_2$ (acetone).
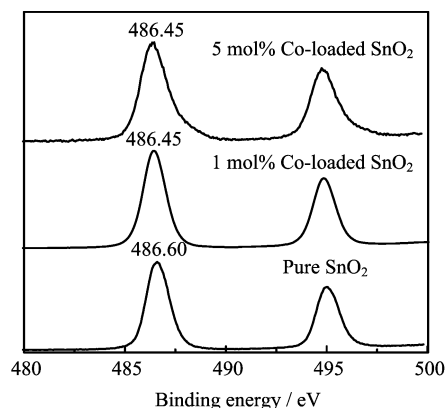


FIG. 4 Gas sensitivity of sensors to several gases (1000 ppm) as a function of Co$_3$O$_4$ content at 300 °C.



FIG. 6 Sn3d$_{5/2}$ XPS spectra of pure and CoO$_{4/3}$-loaded SnO$_2$.

## C. Mechanism

Two types of interactions between additive and oxide semiconductor have been suggested [14]. One type of promoting effect is called chemical sensitization. The gas sensitivity is increased because the additive increases the rate of the chemical processes. Another type is electronic sensitization. The pure oxide semiconductor has a bare surface and surface adsorbed oxygen is utilized for the oxidation reaction. When the additive is added, the additive in the oxidized state induces a surface space charge layer which is strongly depletive of electrons in the oxide near the interface. When the additive is reduced on contact with the reducing gas, it relaxes the space charge layer by giving back electrons to the oxide semiconductor. In this way the gas sensitivity is improved greatly.

As mentioned in introduction, the adsorbed oxygen gets trapped at the grain boundary trap states thereby increasing the space charge region and this results in a decrease in conductance of the material in air. In pure $SnO_2$, this dominates the gas sensitivity. It is known that p-type $Co_3O_4$ has a larger work function than $SnO_2$. When $SnO_2$ and $Co_3O_4$ are mixed together, reflecting electronic interactions take place between $SnO_2$ and $Co_3O_4$. Conduction electrons of $SnO_2$ grains are drawn toward $Co_3O_4$, so the depth of the space charge region in $SnO_2$ grains is expanded. The shift of binding energies of $Sn3d_{5/2}$ and work function of $SnO_2$ could be attributed to the electronic interaction [14,20]. The increase of the work function of $SnO_2$ is also observed from the increase in electrical resistance. Upon exposure to alcohol and acetone, $Co_3O_4$ is reduced more preferentially than $SnO_2$ so that the conduction electrons are given back to $SnO_2$, leading to larger sensor response than pure $SnO_2$.

This type of sensitization has been observed for $SnO_2$ sensors impregnated with $Ag_2O$ [13], and with PdO [14,15]. When exposed to air, all these metal oxides exert an electronic interaction with $SnO_2$. On exposure to reducing gas, they are converted more or less to metals (Ag and Pd respectively) [13-15], resulting in the disappearance of the electronic interaction. Such a change in the oxidation state of the additive is responsible for the promotion of the gas response. The electronic mechanism plays a role in the gas sensing promoter.

## IV. CONCLUSION

The behavior and mechanism of the gas sensing characteristics of $Co_3O_4$-loaded $SnO_2$ have been discussed. Thick films of $Co_3O_4$-loaded $SnO_2$ composites exhibit good response to alcohol and acetone at 300 $^oC$. Though the best operating temperature has not been lowered, the gas response to alcohol and acetone goes through a sharp maximum sensitivity at 5 mol%$CoO_{4/3}$ with a change in $Co_3O_4$ content. The maximum sensor response ($R_a/R_g$) to alcohol or acetone, each 1000 ppm in air, is 301 or 200, respectively, at 300 °C which is about 7 or 5 times as large as that of the pure $SnO_2$. Such strong promotion of sensor response is attributed to an electronic mechanism in the gas sensing promoter. The XPS results also indicate the electronic sensitization. The selectivity to alcohol and acetone over $H_2$ and CO is also promoted by the addition of $Co_3O_4$ to $SnO_2$.

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