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Metal-Oxide Thin Film with Pt, Au and Ag Nano-Particles for Gas Sensing Applications

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In this paper, we report an experimental study carried out to synthesize noble-metal nanoparticles on a polycrystalline ZnO film for gas sensing applications. The necessary process parameters are optimized to achieve the desired morphologies of Pt, Au and Ag nano-particles along with the base layer of ZnO on an alumina substrate. Observations on the formation of nano-particles on the ZnO film are made using scanning electron microscope (SEM) and the results are presented. A detailed study is performed on the formation of nanoparticles on a ZnO film using SEM, and the results are discussed. The responses of the samples with and without nanoparticles are studied with oxygen as test gas. The samples with noble-metal nanoparticles exhibit enhanced sensitivity compared with those without nanoparticles. It is also observed that, with an increase in the operating temperature of ZnO films, the samples show further improvement in sensitivity. In addition, the samples with nanoparticles show fast initial recovery behavior.

1. Introduction

Recently, gas-sensing devices have received much attention for several reasons. There is great interest in developing high-performance gas sensors for various applications such as controlling air pollution and exhaust gases. Among the different types of gas sensor, resistive gas sensors offer the advantages of compact size, simple fabrication, low cost and simple measurement electronics.(1) The simplicity of the fabrication of resistive gas sensors, however, is offset by inherent limitations in selectivity and sensitivity.(2) The relative response to these large families of gases can be tuned through various ways.(3–5) One way to overcome this problem is through the addition of a catalyst. A catalyst of noble-metal nanoparticles can be added with adequate dispersion onto the surface of a

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*Corresponding author, e-mail address: kraj@isu.iisc.ernet.in metal-oxide film.(6,7) The distribution of noble metal nanoparticles on a polycrystalline film plays an important role in increasing the sensitivity and selectivity and decreasing of the operating temperature of sensing devices.(8,9) Therefore, it is necessary to study the effects of process parameters on the morphology of nanoparticles. In this paper, we report our experimental work on synthesizing noble-metal nanoparticles on polycrystalline ZnO films for gas sensing applications. We also report the sensitivity data of ZnO sample films, both with and without nanoparticles, and with oxygen as test gas.

2. Experimental

We used alumina as substrate for gas sensing because of the following advantages: 1) it can withstand high temperatures and 2) it does not react with gas-sensitive films. Zinc oxide (ZnO) thin films with noble-metal nanoparticles were explored for their possible application to gas sensing. The schematic of a gas sensor is shown in Fig. 1. ZnO is a material that can be easily deposited, and its film characteristics can be easily reproduced. However, this material has not yet been extensively explored for gas sensing applications. One of the most promising methods of depositing ZnO films is sputtering. Hence, we used DC reactive magnetron sputtering for the deposition of ZnO films.

The necessary process parameters and information on the deposition system have been described in our earlier paper.(10) In that paper, we described the initial work on synthesizing noble-metal nanoparticles such as Pt, Au and Ag on polycrystalline ZnO films. However, for the convenience of readers, the optimized process parameters for the synthesis of ZnO and noble-metal nanoparticles on ZnO films are shown in Tables 1 and 2, respectively.

The process parameters that control the morphology of the particles on polycrystalline ZnO films are undoubtedly crucial in achieving the desired properties of the gas sensor. It is desirable that the catalyst be dispersed on the surface of the gas-sensing metal oxide, rather than as a continuous film, so that the sensing film will not be electrically shorted by the metal. The agglomeration of a sputtered thin-film layer into particles with optimum dispersion rate and size is very important in the realization of gas sensors.(11) In the form of small particles, the metals have been found to have improved catalytic performance.(1,12,13) This is partly due to the relative increase in surface area. In our study, different combinations of annealing time and temperature defined as the thermal budget (time × temperature) were employed to study their effect on the morphological variation of the nanoparticles obtained from continuous films. In our previous paper, we describe the experimental procedure for the synthesis of noble-metal nanoparticles on ZnO films.(10) The surface morphologies of the particles on the ZnO/alumina were studied by scanning electron microscopy (SEM). The different thermal budgets used in the experiment are summarized in Table 3. In this paper, we present typical images of the samples recorded using SEM.

Because it is impossible to measure the thickness of ultra thin films with a surface profilometer, for the purpose of estimating the deposition rate of noble-metal films, such films were deposited for 10 min on a glass substrate with a sharp-edged mask. The process parameters maintained were the same as those used during the deposition on ZnO for 15 s. The thicknesses of the films on glass samples were measured using a surface profilometer

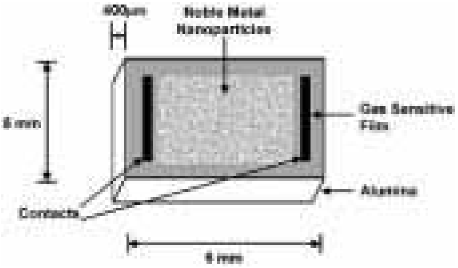


Fig. 1. Schematic of gas sensor with nanoparticles.

Table 1
Optimized sputtering process parameters for deposition of ZnO thin films on alumina substrate.

Process parameter	Value
Base pressure	10^{-5} mbar
Working pressure	1.2×10^{-4} mbar
Inert gas	Used Argon
Target substrate distance	6 cm
Presputtering time	10 min.
Current density	2.26 mA/cm^2
Deposition rate	140 A°/min
Substrate temperature	200°C
Deposition time	30 min

Table 2
Optimized sputtering process parameters for synthesis of nano-particles on ZnO films deposited onto alumina substrate.

Process parameter	Value
Base pressure	10^{-5} mbar
Working pressure	4×10^{-4} mbar
Inert gas used	Argon
Target substrate distance	6 cm
Presputtering time	10 min
Current density	1.13 mA/cm^2
Deposition rate	200 A°/min
Deposition time	15 s

(Talysurf series-5, Taylor Hobson, UK). The deposition rate for all the noble metals, namely, Pt, Au and Ag, was found to be approximately 200 Å/min. From these data, the thickness of ultra thin noble-metal films deposited on ZnO/alumina is estimated to be approximately 50 Å.

To attach electrical leads to the sensing film, silver pads were deposited for ease in soldering. Figure 1 shows the alumina substrate, ZnO film for gas sensing and the silver

Table 3
Combinations of thermal budget (time × temperature) applied to Noble-metal films deposited on ZnO/alumina.

Duration of Deposition	Annealing Time × Temperature
5 s	Annealed in air ambient for 30 min at 600°C
15 s	Annealed in air ambient for 30 min at 300°C
15 s	Annealed in air ambient for 30 min at 150°C
15 s	Subjected to in situ annealing during deposition at 200°C
15 s	Postdeposition annealing in vacuum for 30 min at 200°C
15 s	No annealing, room-temperature deposition

electrodes deposited on either end. The electrodes were deposited using a mechanical mask. This is the direct deposition method of getting patterns of a thin film on a substrate. The mask was placed close to the substrate to obtain the required pattern on the film. In our experiment, the mask used is made of copper of 100 μm thickness. We used DC magnetron sputtering for the deposition of Ag. The silver target was 99.9% pure and 2 mm thick. The sputtering parameters optimized for the deposition of Ag are shown in Table 4.

The gas sensing behavior of the samples, both with and without nanoparticles, was studied. The detection principle of the metal-oxide (resistive) sensors is based on changes in the resistance of a thin film of a metaloxide (semi-conducting in nature) upon adsorption of gas molecules.(1,2) Gas-solid interactions influence the density of electronic species and hence the resistance of the film. ZnO is an n-type semiconductor; under the operating temperature conditions, it is expected to have an electron-depleted surface. Reducing gases, such as CO and H_2, react with the surface removing chemisorbed oxygen and decreasing the size of the depletion region. On the other hand, oxidizing gases such as NO_2 and O_2, increase the size of the depletion region resulting in an increase in resistance. When oxygen concentration in ambient is below the saturation level, metal oxide sensors can be used as oxygen sensors. Thus, sensor resistance can serve as output signal. The sensor output response study was carried out by placing the sample inside a vacuum chamber. The chamber was initially evacuated to a high vacuum and the heater, which is the key component in the controlled operation of the sensor, was simultaneously switched on to reach the desired operating temperature. The heater assembly used consisted of heating elements with mica sheet electrical insulator (iron box heating element) sandwiched between two aluminum plates of 1 mm thickness. Temperature was measured using a thermocouple locate near the substrate. The leads from the sensor for measuring resistance were taken out from the feed-through fitting in the base plate of the chamber and connected to a $5^1/_2$ digit Kiethley multimeter (Model 195A).

3. Results and Discussion

A morphological investigation of noble-metal nanoparticles on polycrystalline ZnO films was carried out using SEM. To start with, we chose an annealing temperature of 600°C and an annealing time of 30 min. The SEM images of the samples with the above

Table 4
Optimized sputtering process parameters for deposition of Ag thin film on ZnO.

Process parameter	Value
Base pressure	10^{-5} mbar
Working pressure	4×10^{-4} mbar
Inert gas used	Argon
Target substrate distance	6 cm
Presputtering time	10 min
Current density	1.13 mA/cm^2
Deposition rate	200 A°/min

combinations of annealing time and temperature are shown in Figs. 2, 3 and 4 for Pt, Au and Ag films, respectively. In all the figures, the right-hand side shows a magnified view of the left-hand side. As can be seen from Fig. 2, the nanoparticles are not well separated from each other as required for gas sensing applications. However, this combination of annealing time and temperature appears to be well suited for Au, as is shown in Fig. 3. However, in the case of the Ag film, no morphology resembling the nanoparticles can be seen (Fig. 4).

In general, it has been observed that a reduction in annealing temperature enables the achievement of a more desirable morphology of nanoparticles applicable in gas sensors. However, different degrees of thermal treatment are required to achieve well-dispersed and distinct nanoparticles on ZnO for different noble-metal films as has been discussed in our previous paper.(10)

Subsequent to the synthesis of noble-metal nanoparticles on ZnO films, the observations of the electrical behavior of the samples as a function of temperature was performed. Upon measuring film resistance from room temperature up to an operating temperature of 200°C, the films showed a typical semiconducting behavior as expected, because of the predominant increase in the number of conducting electrons with the temperature. The observed variations are shown in the Fig. 5. Film resistance started decreasing as the temperature of the sample increased. This figure shows the normalized value plot for the samples with respect to the initial resistance.

The as-deposited ZnO films, i.e; those deposited by in situ annealing at 200°C, were highly unstable in terms of resistance. The resistance of these films exhibiting semiconducting behavior fluctuated. Hence, to overcome this instability in resistance, after the deposition, films were annealed in vacuum for 3–4 h at 200°C. The films subjected to annealing were quite stable and their resistance stabilized after 20–30 min. As the resistance of the films stabilized, oxygen gas was introduced in steps into the chamber through a needle valve. The corresponding change in the resistance of the films was noted using a $5^1/_2$ digit Kiethley multimeter (Model 195A). The observed behavior is shown in Fig. 6. This observation was made at three temperatures. The change in resistance, and hence sensitivity, was largest at 230°C. As can be seen in Fig. 6, the variation in resistance at a 125°C sample temperature is negligible. Subsequently, the response of the samples with nanoparticles of Pt, Au and Ag on ZnO films was studied with oxygen as test gas. To compare different samples for sensitivity, resistance was normalized with respect to the initial resistance of the sample.

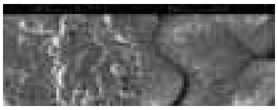


Fig. 2. SEM images of nanoparticles of Pt on ZnO film deposited at room temperature and annealed in air at 600°C for 30 min.

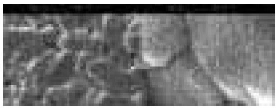


Fig. 3. SEM images of nanoparticles of Au on ZnO film deposited at room temperature and annealed in air at 600°C for 30 min.

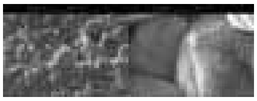


Fig. 4. SEM images of nanoparticles of Ag on ZnO deposited at room temperature and annealed in air at 600°C for 30 min.

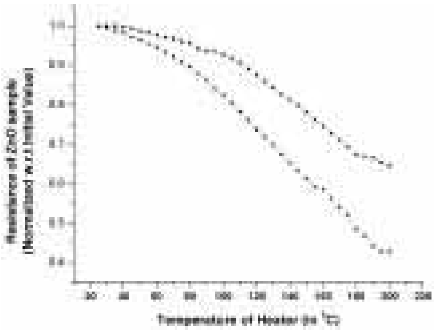
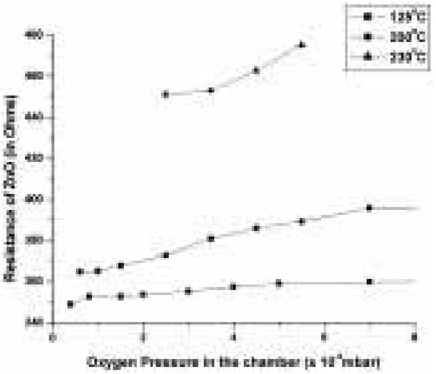


Fig. 5. Normalized plot showing semiconducting behavior of ZnO films on alumina substrates for two samples with different initial resistances.

The effect of nanoparticles on sensitivity is evident from the variations shown in Fig. 7. The change in film resistance with respect to its original value is greater in the case of a ZnO sample with Pt nanoparticles than in the case of other samples. The film without nanoparticles shows the lowest sensitivity.

The recovery behavior of all the samples is shown in Fig. 8. In this figure, the resistance was normalized with respect to the initial resistance of the sensor (the resistance after showing semiconducting behavior and before oxygen gas is injected into the chamber). As can be seen from Fig. 8, the initial recovery is fast in the case of a sample with noble-metal nano-particles, compared with a sample without nanoparticles. However, all samples recover close to the original resistance.



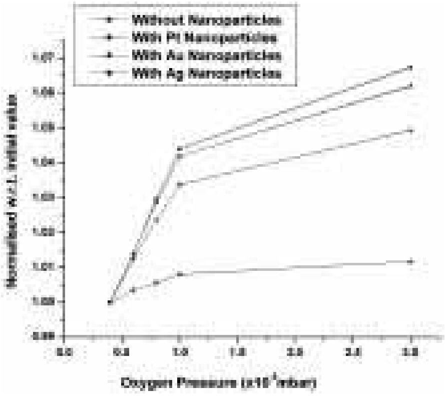


Fig. 6. (left) Variation in resistance of ZnO film upon exposure to oxygen gas at different temperatures.

Fig. 7. (right) Resistance variation of ZnO films with and without nanoparticles normalized to the initial resistance.

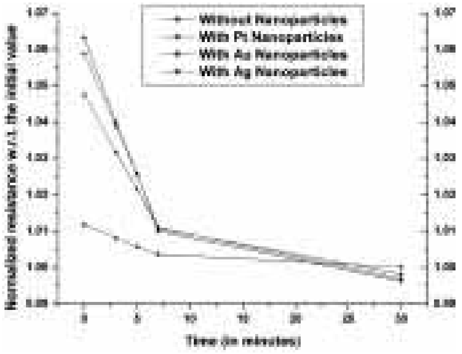


Fig. 8. Recovery of ZnO samples with and without nanoparticles normalized to the initial resistance.

4. Conclusion

A detailed study of synthesizing noble-metal nanoparticles on metal oxide films for gas sensing applications using thin film technology has been carried out. Different degrees of thermal treatment are required to achieve well-dispersed and distinct nanoparticles on ZnO for different noble-metal films. A study of the resistance variation of these samples with and without nanoparticles has been carried out with oxygen as test gas. The film samples with noble metal nanoparticles show enhanced sensitivity compared with the samples without nanoparticles. It has also been observed that, with an increase in the operating temperature of ZnO films, the samples exhibit further improvement in sensitivity.

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