Structural, optical and gas sensing properties of barium titanate surface modified by nano silver

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Abstract: Paper represents the results of SO2 sensing performance of BaTiO3 surface modified by nano silver. Surface modification was performed by dipping of BaTiO3 thick films in the synthesized nano silver. The main objective was to investigate the effect of nano silver on gas sensing performance of BaTiO3 perovskite. Different intervals of dipping time were used to find the optimum dipping amount on the surface of perovskite oxide. Synthesized silver was characterized by UV-visible spectroscopy and transmission electron microscopy. Surface modified thick films were analyzed for structural, morphological, electrical and gas sensing properties by XRD, SEM with EDX, static gas sensing unit respectively. Selectivity of surface modified BaTiO3 thick films was also investigated.

Keywords: Nano silver, surface modification, BaTiO3 thick film, gas sensor.

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I. INTRODUCTION

A number of perovskite-type oxides have been used as gas sensor materials due to their semi-conductive properties and the flexibility of doping and the ease of formulation adjustment [1]. These materials can be obtained either in pure or in doped formulations. Doping flexibility allows controlling of ion transport properties of perovskites and its adsorption/desorption behavior. This advantage is useful to optimize sensor performance.

Perovskite with a general formula of ABO3 is a large family of crystalline mixed oxides. Perovskite was observed, for the first time, in Russian mountains by Gustav Rose in 1839. Irish crystallographer, Helen Dick McGas, has published X-ray diffraction data on barium titanate having perovskite structure [2]. Early attraction on perovskite oxide application was in the field of catalyst [3]. Their stability and activity as an automotive exhaust catalyst encouraged researchers to study their structures, applications, solid-state chemistry and etc. to explore new candidates for specific catalytic demands and then commercialize them. Early results on the catalytic activity of perovskite and their semiconductor behavior encouraged researchers to test them as sensing materials [4,5].

Gas sensing is a multidisciplinary field which requires fundamental investigation and study on its theoretical and experimental surface chemistry and physics. Understanding of solid-state chemistry and gas sensing parameters such as conductivity, adsorption properties, doping effect and etc. could help to develop a conceptual framework to have a high-performance gas sensor.

Obayashi et al. have found the first perovskite gas sensor to detect ethanol [6]. Their early observations on the electrical resistivity increasing of perovskite-type oxide in the presence of ethanol led them to test perovskite materials as a gas sensor. They chose (La,M)BO3 (La=lanthanoid element, M=alkaline earth metals, and B=transition metal) which had good oxidation-reduction catalyst properties. Their preliminary results showed that B ions in a perovskite-type structure can play an important role in gas sensing mechanism. They have noticed that the activity of ethanol sensors with Fe, Co, Ni ion in B site was good while Mn in this position did not show a good activity. The Fe-containing sample showed the highest response ratio, while Co-containing one showed the shortest response time. In the literatures, response ratio or sensitivity is referred to the relative electrical resistance changes in the presence of a target gas [7].

Nanostructured materials, due to their high specific surface area and low particle size, offer an excellent potential for a substantial increase in the performance of gas sensors [8]. In these materials, the depth of the depletion layer is comparable to the particle size, and it could be extended to the whole particle. Any small interaction of gas-solid at the surface of the material may therefore cause a big change in its overall conductivity resulting in a high
response ratio. Gas sensing performance of a nanostructured MO sensor could further be improved by doping with other elements such as noble metals [9,10].

There are numerous reports dealing with improving the sensitivity, selectivity, and optimum sensing temperature of MO by adding noble metals where they play the role of a catalytic agent on the sensing layer. Eranne et al have provided a literature review on pure and doped MO as gas sensing materials [9]. They have concluded that by adding noble metals to the MO gas sensor, sensing temperature could be reduced. Reducing the sensing temperature is an important issue not only to have a low-cost sensing system (heater integration, operation facilities, etc.) but also to improve the stability and long-term performance of the sensors. High temperature working conditions reduce surface area and increase the mean particle size resulting in degradation of sensor performance.

Increasing the selectivity of MO gas sensors is another big challenge. By adding noble metals, tin oxide has shown good sensitivity to CH4 and CO separately, but the low selectivity between CO and CH4 or any other reducing gases still remains a major issue to be addressed [9,11].

Since the catalytic activity and gas adsorption properties of perovskite-type oxides depend strongly on the nature of B-site cations, the selection of B-site will affect their gas sensing properties. In his review paper and based on a number of published works, Fergus [7] concluded that Co and Fe as B-site cations result in a better CO and CH4 sensing properties than the other transitional metals. Moseley et al [12] reported the gas sensing properties of LaFeO3-based perovskite at a temperature range of 400-550°C showing a response ratio of approximately 30% while exposed to 300 ppm CH4.

In this paper, we used chemically synthesized Ag nanoparticles which are used for the surface modification of BaTiO3 (BT) thick films. Besides, as the base material, BaTiO3 powders are synthesized by co-precipitation method[13]. The influence of Ag nanoparticles on the gas sensing properties of BaTiO3 thick films was mainly investigated. This is the first time that Ag nanoparticles are used for the surface modification of BaTiO3 thick films. No considerable data exist in SO2 sensing properties of perovskite-type barium titanate surface modified by nano silver.

II. EXPERIMENTAL DETAILS

A. Synthesis of BT and Preparation of BT Thick Films

BaTiO3 fine submicron powders were synthesized from Ba(OH)2 and TiCl4 using a coprecipitation process and thick films were prepared as described elsewhere [13].

B. Synthesis of Silver Nanoparticles

The silver nanoparticles with well dispersion were prepared by reducing AgNO3 with hydrazine hydrate solution. For the synthesis of silver nanoparticles, silver nitrate solution and Sodium Dodecyl Sulphate (SDS) were used as a metal salt precursor and a stabilizing agent, respectively. Hydrazine hydrate solution used as a reducing agents. Solution of silver nitrate AgNO3 was prepared by dissolving 0.0169g of silver nitrate in 100 ml of distilled water. 20 ml of silver nitrate solution was kept in hot plate at 90°C for 5 minutes and then add 2.5 ml of SDS drop by drop once the reduction process begins colour change appears. The transparent colourless solution was converted to the characteristic pale yellow-brown in addition of hydrazine solution used as reducing agent. The occurrence of colour was indicated the formation of silver nanoparticles [14]. This solution was used for further characterization and surface modification of BT thick films.

C. Preparation of Nano Ag Surface Modified BT Thick Films

The thick films of BT from as-prepared powders were surface modified with Ag nanoparticles by dipping of BT thick films in solution of synthesized silver nanoparticles. In order to compare gas sensing performances, thick films were dipped for different interval timing as 5 min, 10 min, 15 min, 20 min and 30 min and referred respectively as AgBT5, AgBT10, AgBT15, AgBT20 and AgBT30. These films were dried at 100 °C, followed by firing at 550 °C for 30 min and then used for further characterization such as UV-visible spectroscopy, scanning electron microscopy, XRD and tested their gas sensing properties.

D. Characterization and Gas Sensor Test

Phase analysis and crystallite size determination were performed by powder X-ray diffraction (XRD) with Cu/Kα radiation (λ = 0.154 nm). Scanning was performed between 20° and 80° and the diffractogram were recorded. The Debye-Scherrer equation was used to calculate the average crystallite size (D). Microstructure and morphology of the synthesized powders and surface modified samples were investigated using scanning electron microscopy (SEM).

Gas sensing tests were performed in a reactor consisting of a glass chamber with a capacity of 1000 ml, a heating system with theremocouple to adjust the chamber’s temperature [15]. Sample conductivity was first measured under dry air at different temperatures. A mixture of air and 100 ppm gas was then introduced into the chamber while the sample resistance was continuously recorded. To repeat the experiment, the temperature was then increased to 450°C for 5 min under dry air. This step is called “recovery step” during which all gas molecules are desorbed from the surface of the sample. The response ratio was calculated using the following equation:

\[
\text{Response ratio} (\%) = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \quad (1)
\]

where \( R_{\text{gas}} \) is the resistance under a given gas concentration at constant temperature and, \( R_{\text{air}} \) is the base resistance at constant temperature under gas-free atmosphere (dry air). Gas testing procedures, including the recovery step, were repeated several times to verify the repeatability of the responses.

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III. RESULTS AND DISCUSSION

A. XRD Analysis

Fig. 1 shows the XRD pattern of the BaTiO$_3$ powder prepared by co-precipitation. In Fig. 1, there is no phase other than BaTiO$_3$ discovered in the XRD pattern. Fig. 2 shows the XRD pattern of BT modified with silver, no phases other than BaTiO$_3$ and silver are observed, which is consistent with standard powder diffraction data of JCPDS, No. 05-0626 [16]. This means that no reaction takes place between BaTiO$_3$ and silver during dipping and sintering process. The average crystallite sizes were calculated using the full width at half maximum FWHM using the Scherrer equation and found to be 15 nm and 30 nm for pure BT and AgBT30 respectively.

![Fig. 1. XRD pattern of BaTiO$_3$ powder](image1)

![Fig. 2. The XRD pattern of Ag-BT30](image2)

B. Characterization of Nano Ag By UV-Visible Spectroscopy and Transmission Electron Microscopy

UV-visible spectroscopy is one of the most widely used techniques for structural characterization of silver nanoparticles. The absorption spectrum (Fig. 3) of the pale yellow-brown silver colloids prepared by hydrazine reduction showed a surface plasmon absorption band with a maximum of 418 nm designating the presence of spherical or roughly spherical Ag nanoparticles, and TEM imaging corroborated this (Fig. 4(a)). This image show agglomerates of minuscule grains and some dispersed nanoparticles with the particles range in size from 2 to 6 nm diameter. The corresponding SAED pattern of silver particles is shown in Fig. 4(b). When the electron diffraction is carried out on a limited number of crystals one observes only some spots of diffraction distributed on concentric rings.

![Fig. 3. UV-Vis absorption spectra of nano Ag](image3)

![Fig. 4 (a)](image4a)

![Fig. 4 (b)](image4b)

C. Surface Morphology by Scanning Electron Microscopy Analysis

The surface morphology of pure BT and surface modified AgBT are shown in Fig. 5 (a-f). As is shown in Fig. 5(a), the grains are relatively uniform with small amount of bigger grains and the average grain size is about 0.2 µm. Interestingly, there are many small silver particles (size range > 0.1 µm) observed in Fig. 5(b). The formation
of small silver particles can be explained that they condensate on the surface of the BT during the dipping process.

![Fig. 5(a) Pure BT](image)
![Fig. 5(b) AgBT5](image)

![Fig. 5(c) AgBT10](image)
![Fig. 5(d) AgBT15](image)

![Fig. 5(e) AgBT20](image)
![Fig. 5(f) AgBT30](image)

Fig. 5. SEM images of (a) pure BT and (b-f) nano Ag surface modified BT thick films

**D. Elemental Analysis by EDX**

The EDX analysis of the pure BT and surface modified Ag-BT is shown in Fig. 6(a-f). From EDX analysis, silver exists on the surface of BT and peaks are observed in Fig. 6(b-f). As dipping time increases, there is increase in wt % of silver on surface of BT.

![Fig. 6(a) Pure BT](image)
![Fig. 6(b) AgBT5](image)

![Fig. 6(c) AgBT10](image)
![Fig. 6(d) AgBT15](image)

![Fig. 6(e) AgBT20](image)
![Fig. 6(f) AgBT30](image)

Fig. 6. EDX spectra of (a) pure BT and (b-f) nano Ag surface modified BT thick films

**TABLE I. TABLE TYPE STYLES**

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**E. Electrical Characterization of Pure BT and Ag-BT Thick Films**

**a) I–V Characteristics of Pure BT And Ag-BT Thick Films**

I–V characteristics of pure BT and Ag-BT thick films are displayed in Fig. 7. A good ohmic contact was ensured for above films by applying silver paste on surface of the thick film. From figure nonlinear contact behavior was observed for pure BT and Ag-BT thick film samples.

![Fig. 7](image)

Fig. 7. I–V characteristics of pure BT and Ag-BT thick films

**b) Electrical Conductivity of Pure BT and Ag-BT Thick Films**

Fig. 8 shows the temperature dependent conductivity of pure BT and Ag-BT thick films, exhibiting semiconducting behavior in the whole measured temperature range. The measurements were carried in the temperature range of RT–450 °C. Electrical conductivity of these films goes on increasing with increase in temperature in air ambient, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the films. The conductivities of samples made with surface modified BT were enhanced by surface modified by nano Ag compared with pure BT. The increase in conductivity may be due to the enhancement of the electron concentration by Ag donors. In figure, the AgBT5 sample
showed the highest conductivity in a given temperature range. However, a further increase in dipping time resulted in a systematically decrease of the conductivity. This phenomenon can be attributed to the buildup of space charge potential barriers across the grain boundaries [17].

**F. Gas Sensing Properties of Pure BT and Ag-BT Thick Films**

**a) Variation of Sensitivity with Operating Temperature**

Fig. 9 shows the variation in the sensitivity of H₂S (100 ppm) with operating temperatures ranging from 50°C to 450°C. It is noted from the graph that sensitivity increases with increasing temperature, attains a maximum at 250°C, and decreases with further increase in operating temperature. Fig. 10 shows the sensitivity of pure BT sensor dipped for 30 min to SO₂ gas at operating temperature 200°C. At 30 min dipping time, the sensor would find Ag (0.57 wt%) to be optimum. The optimum wt% of Ag (0.57) would cover the film surface uniformly. As wt% of Ag increases, sensitivity increases due to higher wt % of Ag surfactant available on the base material to react with the gas molecules. The largest sensitivity in case of the sample (30 min) may be because of more available sites (misfits). The surface of nano-Ag misfit regions enhances the oxygen adsorption on the surface. Thus the number of oxygen species adsorbed on the activated surface would be larger. The larger the number of oxygen species adsorbed, the faster the oxidation of SO₂ gas would be. The pure BT sensor showed the highest sensitivity to H₂S, while nano-Ag surface-modified sensor showed it to SO₂ gas. The alteration in nature of gas sensing response from H₂S to SO₂ gas for the nano-Ag surface modified BT sensor could be largely due to possibility of formation of silver sulphide more easily than formation of silver oxide [18]. This would increase the conductance of the film crucially, enhancing sensitivity.

**b) Selectivity of Pure BT and Ag-BT Thick Films**

Fig. 12 shows the histogram showing selectivities of pure BT and Ag-BT thick films. It is clear from the histogram that pure BT is more selective to H₂S while Ag-BT is more selective to SO₂ gas. Ag misfits on the surface of BT thick film seem to be responsible for the shift in selectivity from H₂S to SO₂ gas [19].
using dipping technique is an effective method for improvement of sensitivity of BT based gas sensors.

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