Influence of pH on structural and electrical properties of sol-gel derived (Ba, Sr)TiO thin films under humid conditions

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Abstract

Polycrystalline (Ba, Sr)TiO (BST) thin films were prepared by the sol-gel technique using titanium isopropoxide and 2-ethyl hexanoate precursors for barium and strontium. The pH value of the precursor sol was adjusted by adding ammonium hydroxide. These films were studied at 7.4 and 9.0 pH and at different molarities ranging from 0.15 to 0.30 M. The films were porous and absorb water vapour when exposed to a humid environment. The glancing angle X-ray diffraction (GAXRD) pattern clearly shows a preferential orientation of crystallites in (110) direction with increase of pH. Atomic force microscopy (AFM) shows that grain size decreases from 67 to 38 nm with the increase of pH from 7.4 to 9.5, while surface roughness decreases from 0.81 to 0.74 nm. We have found that sensitivity, linearity and response time of the humidity sensor utilizing these films can be improved by tailoring the process parameters such as pH and molarity of the precursor sol. The calculated sensitivity is found to be 46 at 0.30 M, which is higher as compared to the values 40 and 15 at 0.15 M and 0.20 M, respectively, for a given 7.4 pH of sol. As we increase the pH of sol, it was observed that sensitivity of the deposited films increases and reaches to the maximum value (approx. 189) at 9.0 pH.

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Keywords: BST thin film; Sol—gel; AFM; Humidity sensor; pH of sol

1. Introduction

Humidity sensors are of increasing interest in electronic control systems. A wide variety of ceramic polymeric and composite materials have been used for humidity sensors. Sensors based on polymeric and composite materials have a limited temperature and humidity range. Moreover, the response and recovery rates are generally slow. Ceramic humidity sensors based on porous materials show higher mechanical and chemical resistance, wide range of operating temperature and rapid response to change of humidity. Porous ceramic materials exhibit change in their electrical properties such as capacitance-conductance on exposure to humid environment due to adsorption of water molecules into the pores of ceramic materials through capillary action.

The ceramic humidity sensors fabricated using bulk or thick film technology, have not yet reached a high technological level. The conventional ceramic technique has some obvious disadvantages. It is difficult to prepare high purity ceramic material with homogeneous distribution of components and pores, and secondly, it always needs very high temperatures (≥1200 °C) to sinter the material. The solution to this problem is the thin film form of the sensing element, which is also compatible with the present trend of the integrated sensor research. The requirements of a good humidity sensor are high sensitivity and selectivity over a wide range of humidity and temperature, fast response time and stability over a long period of operation.

We have earlier reported that (Ba, Sr)TiO (BST) thin films can be used as humidity sensors. It is well known in perovskite materials that the anion site (Ba^{2+}) is susceptible to humidity. Several authors have tried to improve the sensitivity and linearity of humidity sensors by doping the ceramic material with...
different elements such as Li, K, MgO, etc. Recently, we have been successful in improving the sensitivity and linearity of sol-gel prepared thin film humidity sensors by optimising the process parameters. It is known that the pH of sol has a large effect on the structural properties of sol-gel synthesized materials. Both high and low pH can accelerate the process of sol-gel formation. However, the characteristics and properties of a particular sol-gel derived inorganic network are also related to a number of other factors that affect the rate of hydrolysis and condensation reactions, such as temperature and time of reaction, reagent concentrations, catalytic nature and concentration, HO\textsubscript{2}YTi molar ratio (R), aging temperature and time for drying. Among these factors, pH, nature and concentration of the catalyst, HO\textsubscript{2}YTi molar ratio (R), and the temperature have been identified as most important. Thus, by controlling these factors, it is possible to vary the structure and properties of the sol-gel derived inorganic network.

The X-ray diffractometry (XRD) patterns reveal that these films are polycrystalline in nature. A preferred orientation of crystallites in (110) direction is observed at 9.0 pH. Atomic force microscopy (AFM) was used to study these films at different pH to obtain information about growth and surface morphology. We have found from these micrographs that grain size decreases with the increase of pH. Electrical measurements have been performed on metal-insulator-metal (MIM) structure at different humidity levels.

2. Experimental

BST thin films were prepared by sol-gel technique, which has the advantages such as simplicity, excellent homogeneity as well as relatively low processing temperatures and precise microstructure control of the deposited films. These films were deposited with thick-
ness of 0.6 mm on stainless steel (SS) substrates at room temperature. Barium and strontium hexanoates and titanium-isopropoxide were used as precursors for Ba, Sr and Ti, respectively. A small quantity of acetylacetone was added to increase the stability of sol. The flow chart of the experimental procedure is shown in Fig. 1. These films were annealed at 700°C for 1 h in air to get the perovskite phase. For electrical measurements, circular gold (Au) dots of 1-mm diameter were deposited by thermal evaporation process.

A 12 kW rotating anode X-ray diffractometer with Cu Kα (l s 1.54 Å) radiation (model Giegerflex-Dymax-RB-RU200, Rigaku, Japan) was used for crystallographic studies. X-Ray diffraction pattern was taken in the range of 20-60° at a glancing angle of 28. Surface morphology of these films was investigated by using Cambridge Instruments S320 scanning electron microscope (SEM), operated at 20 kV and atomic force microscopy (contact mode) using the Nanoscope II (Digital Instrument, Inc., USA). The film thickness was measured using stylus type instrument Talystep (Rank Taylor Hobson Ltd., UK). The capacitance was measured at different humidity levels by using LCR meter (Systronics 928 LCR-Q tester).

3. Results and discussions

3.1. Micro structural studies

Glancing angle X-ray diffraction (GAXRD) patterns for BST thin films at different pH of sol were shown in Fig. 2. These patterns reveal the polycrystalline nature of BST thin films. Normally, the maximum intensity is observed for (110) reflection with however, a preferential orientation of crystallites in (110) direction with increase of pH gives much higher intensity for this reflection.

3.2. AFM study at different pH

Scanning electron micrograph (SEM), shown in Fig. 3, indicates that these films are continuous and porous in nature and, therefore, adsorb water vapor when

Fig. 2. Glancing angle X-ray diffraction pattern of BST thin film at different pH (a) 7.4 and (b) 9.0.

Fig. 3. SEM micrograph of BST thin film of thickness 0.60 mm at magnification of 15 K.
3.3. Humidity sensing characteristics

For a material to be a good humidity sensor, the desired parameters are high sensitivity, good linearity, reversibility, fast response time, long life, small chemical and thermal dependence. In the following section, we have explained the effect of processing parameters such as molarity and pH of sol on sensitivity, linearity, response and recovery time as described below.

3.3.1. Effect of molarity

We have defined the sensitivity ($S$) of humidity sensor as the ratio of change in capacitance from 0% RH to 98% RH to the capacitance at 0% RH and can be written as follows.

\[ S = \left( \frac{\Delta C}{C_0} \right) = \left( \frac{C_{\text{98\%RH}} - C_{\text{0\%RH}}}{C_{\text{0\%RH}}} \right) \times 100 \]

Fig. 5 shows the capacitance vs. relativity humidity plot at different molarities at 7.4 pH. When we increase the molarity from 0.15 to 0.30 M at a fixed pH of 7.4, the sensitivity is found to be maximum at 0.30 M (Table 1). It is calculated to be 46 at 0.30 M, which is higher as compared to the values 40 and 15 at 0.15 M and 0.20 M, respectively. It shows that with the increase of molarity for the same thickness of film, the void fraction increases with the increase of molarity, which improves the sensitivity of humidity sensor at higher molarity.

For a good humidity sensor, it is desirable that the sensing characteristic of the sensor is linear over the humidity range of interest. Various studies on different ceramic materials reveal that radius of pores in the active ceramic material in the range of 0-300 Å are necessary for obtaining higher sensitivity in the low humidity region which in turn helps to linearise humidity sensing characteristics. We have plotted capacitance data on log scale at 7.4 pH and used the linear fit programme to fit our experimental data, which is shown in Fig. 6. It is observed that linearity is also improved with higher molarity.

3.3.2. Effect of pH

The pH of the sol can affect the hydrolysis and condensation reactions of sol-gel process as given below. If pH of sol is greater than seven (pH 7) then base-catalysed hydrolysis of Ti alkoxides proceeds much more slowly than acid-catalysed hydrolysis at an equivalent catalyst concentration. It is likely that water dissociates to produce hydroxyl anions under basic conditions. The hydroxyl anion then attaches to the Ti

exposed to humid environment. Atomic force micrographs (AFM) at pH 7.4, 9.0 and 9.5 are shown in Fig. 4. These micrographs clearly show that grain size decreases from 67 to 38 nm with the increase of pH from 7.4 to 9.5, while surface roughness decreases from 0.81 to 0.74 nm. There is agglomeration of sol particles at lower pH. As the pH of sol is increased, this tendency of agglomeration decreases with pH. It means that grain size decreases with the increase of pH.

Fig. 4. Atomic force microscopy (AFM) micrographs at different pH (a) 7.4, (b) 9.0 and (c) 9.5.
atom. In other words the -OH ion displaces -OR with inversion of Ti tetrahedron as given below.

\[
\begin{aligned}
H_2O \rightarrow H^+ + OH^- \\
\text{[Ti-OR + OH$^-$ $\rightarrow$ [R-O-Ti-O-H]$^+$ $\rightarrow$ R-O-Ti-O-H]} \\
\end{aligned}
\]

High pH accelerates condensation reactions also. For the pH in the range between 2 and 6, the condensation rates are proportional to OH ion concentrations. Condensation occurs between more highly condensed species and those less highly condensed and somewhat neutral species. However, above pH 7, condensed species are ionized and, therefore, mutually repulsive. The most widely accepted mechanism for the base-catalysed condensation reaction involves the attack of nucleophilic deprotonated Ti as given by following equation:

\[
\begin{aligned}
\text{[Ti-OH} + \text{Ti-O$^-$} $\rightarrow$ \text{[Ti-O-Ti-O$^-$] + OH$^-$]} \\
\end{aligned}
\]

Therefore, higher pH increase deprotination and surface charges, thereby postponing the aggregation and gelation steps. Hence, the grain size decreases with the increase of pH of sol. In other words, high pH preparations yield larger void fractions, larger average pore diameter, and larger specific area. In other words, we can say that higher the pH, more will be the porosity yield sensitivity and fast response and recovery of the humidity sensor.

After fixing the molarity of sol at 0.30 M required for good humidity sensing properties, we have studied the effect of pH variation. As we increase the pH of the solution, it was observed that sensitivity of the deposited films increases, shown in Fig. 7 and reaches to the maximum value (approx. 189) at 9.0 pH. The values of sensitivity factor at different molarities and pH are tabulated in Table 1.

<table>
<thead>
<tr>
<th>Molarity (M)</th>
<th>Sensitivity (%S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7.4</td>
<td>pH 9.0</td>
</tr>
<tr>
<td>0.15</td>
<td>40</td>
</tr>
<tr>
<td>0.20</td>
<td>15</td>
</tr>
<tr>
<td>0.30</td>
<td>46</td>
</tr>
</tbody>
</table>

Fig. 5. Humidity sensing characteristics at given pH 7.4 and different molarity of sol (a) 0.15 M, (b) 0.20 M and (c) 0.30 M.
Fig. 6. Log plot and linear fit for humidity sensing characteristics at given 7.4 pH and different molarity of sol (a) 0.15 M, (b) 0.20 M and (c) 0.30 M.

Fig. 7. Humidity sensing characteristics at given molarity 0.30 M and different pH of sol (a) 7.4 and (b) 9.0.

Fig. 8. Log plot and linear fit for humidity sensing characteristics at given molarity 0.30 M and different pH of sol (a) 7.4 and (b) 9.0.
Table 2
Effect of pH on the response and recovery time

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>pH 7.4</th>
<th>pH 9.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Response time</td>
<td>7.902</td>
<td>3.610</td>
</tr>
<tr>
<td>Recovery time</td>
<td>8.230</td>
<td>5.046</td>
</tr>
</tbody>
</table>

The effect of pH on linearity of sensor is shown in Fig. 8 at 7.4 pH and 9.0 pH. It is observed that the linearity of humidity sensor is also improved with the increase of pH. The effect of pH change on response and recovery time is shown in Fig. 9. The response and recovery time has been defined as the time taken to show 90% of overall variation in relative humidity. Adsorption is an exothermic process, whereas desorption needs external energy for water molecules to depart from the metal oxide surface w13x. Therefore, a relatively long time seems to be required to disorbe the water vapor i.e. recovery time should be higher than response time. Fig. 9a,b show the humidity response curve corresponding to water adsorption and desorption at different pH values of sol. The values of response and recovery time calculated from the adsorption and desorption curves at 7.4 and 9.0 pH are given in Table 2. With the increase of pH of the sol, the response and recovery time are found to decrease. The response and recovery time are calculated to be 3.6 and 5.1 s at 9.0 pH. From this study it is concluded that at 9 pH, the humidity sensor shows excellent time response.

4. Conclusions

In the present study we have found that the humidity sensing characteristics of BST thin films made by sol-gel technique are critically dependent on molarity and pH of precursor sol. We have optimised these process parameters to get better sensitivity; linearity and fast response time for BST thin films for their humidity sensor application. The sensitivity to humidity for these films is maximum at 0.3 M at 9 pH. The linearity and time response of humidity sensor using BST thin films under these conditions, is acceptable for a good humidity sensor.

References

w7x M. Prudenziati, B. Morten, Sensor. Actuat. 10 (1986) 379.
w17x Kenneth.Mauritz sol-gel research, pp. 1-10.