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Study on the Characteristics of Ag Doped CuO-$BaTiO_3$ CO_2 Sensors

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Abstract: In this paper the characteristics of a CuO-$BaTiO_3$ based CO_2 gas sensor was investigated. The sensitivity of the CuO-$BaTiO_3$ based CO_2 sensor was influenced by doping various metal elements such as Au, Ag, Pt, Pd, Ce, Mg, Sr, La, Zn, Fe and Bi, which were added as a pure metal or in the form of metal oxides. It was found that Ag is the most suitable additive among all substances tested. The Ag-doped CO_2 gas sensor has better sensitivity and lower operating temperature, with a detection concentration range of from 100 ppm to 10%. The sensor also shows good stability.

Keywords: Gas sensor, CO_2 sensor, Solid ion electrolyte, Sensitivity, Doping

Introduction

The CO_2 level in the atmosphere has been increasing and has brought about global warming. Infrared technology has been widely used in CO_2 detection, but the technology is disadvantageous because IR instruments are usually large and expensive. A simple and cheap method of CO_2 detection is thus needed. Potential methods for CO_2 detection are gas sensors based on measuring potentiometric[1-12] or amperometric[13] responses, or measuring capacitance[14,15] or resistance change[16].

In this paper a CuO-$BaTiO_3$ based CO_2 gas sensor was prepared. The gas- sensitive characteristics of the sensor were studied. It was found that Ag is the most suitable additive among all metal elements

tested. The Ag- doped CO_2 gas sensor has better sensitivity and lower operating temperature, and good stability. The detection concentration range is 100 ppm to 10% CO_2.

Experimental

Appropriate amounts of $BaCO_3$ and TiO_2 (1:1 in molar ratio) were mixed thoroughly in an agate mortar. The mixture was heated at 1300°C for 6 hours in air and then ball milled. The powder, $BaTiO_3$, was then mixed with CuO in 1:1 molar ratio thoroughly. Doping elements were added in corresponding nitrate. The mixture was made into pellets and was sintered at a certain temperature for 5 hours in air.

The CuO-$BaTiO_3$ based sensor has two electrodes made of a precious metal such as Pt , Au or Ag. The electrodes are in solid contact with the CuO-$BaTiO_3$ composite material. Resistance of the sensor was measure both in air (R_a) and in CO_2 gas (R_g). Gas sensitivity S is defined as $S = R_g/R_a$.

Results and Discussion

Influence of Doping Elements on CO_2 Sensitivity and Operating Temperature

The adulteration with noble metal or metal oxide has influence on sensitivity and operating temperature of the CuO-$BaTiO_3$ sensor, as is shown in table 1. The doping ratio is 1% mol. Doped materials were heated at 500°C for 5 hours and were then used to make the sensor. The sensitivity is measured in CO_2 of 5000 ppm (or 0.5%) concentration. It can be seen from table 1 that almost all doping elements increased the operating temperature of the sensor. Some impurities such as Au, Fe_2O_3 and CeO_2 decrease sensor's sensitivity to CO_2, but most others including Ag, Pd, SrO, La_2O_3, ZnO and Bi_2O_3 increase it, especially Ag, ZnO, La_2O_3 and Bi_2O_3 have greater effects. It is also observed that when such alkalescency oxide as ZnO, Bi_2O_3, SrO, La_2O_3 is adulterated, the sensor has better sensitivity but also higher operating temperatures typically over 550°C. This is disadvantageous in practical use because the sensitivity will decrease after the sensor has been operated at high temperature for a long time. When adulterated with Fe_2O_3 and Bi_2O_3, the sensor has a lower resistance in CO_2 than in atmosphere. But when adulterated with others the sensor showed the opposite behavior. Based on the results in table 1, a conclusion is drawn that the CuO-$BaTiO_3$ sensor doped with Ag has higher sensitivity and lower operating temperature. This sensor was then selected for further investigation.

R-T and T-S Characteristics of Ag^- Doped CuO-$BaTiO_3$

Fig. 1 shows the relationship between the operating temperature and the resistance of the Ag- doped CuO-$BaTiO_3$ sensor in atmosphere. It shows that CuO-$BaTiO_3$ is one of the typical NTC semiconductor materials. The resistance of the doped material changes greater with temperature than other materials, even at high temperatures. This significant temperature dependence requires the sensor to be operated at a stable operating temperature.

Table 1. The CO_2 sensitivity of doped CuO-$BaTiO_3$ sensor.

Doping substances	**Operating temperature (^oC)**	**R_g(MΩ)**	**R_a(MΩ)**	**R_g/R_a**
/	420	5.65	4.48	1.26
Au	440	12.7	10.7	1.19
Ag	430	0.54	0.34	1.59
Pt	490	5.71	4.53	1.26
Pd	540	10.3	7.46	1.38
CeO_2	530	0.38	0.29	1.31
MgO	580	0.97	0.77	1.26
SrO	580	1.23	0.83	1.48
La_2O_3	600	2.58	1.70	1.52
ZnO	550	4.83	2.91	1.66
Fe_2O_3	440	1.41	1.50	0.94
Bi_2O_3	640	9.78	16.03	0.61

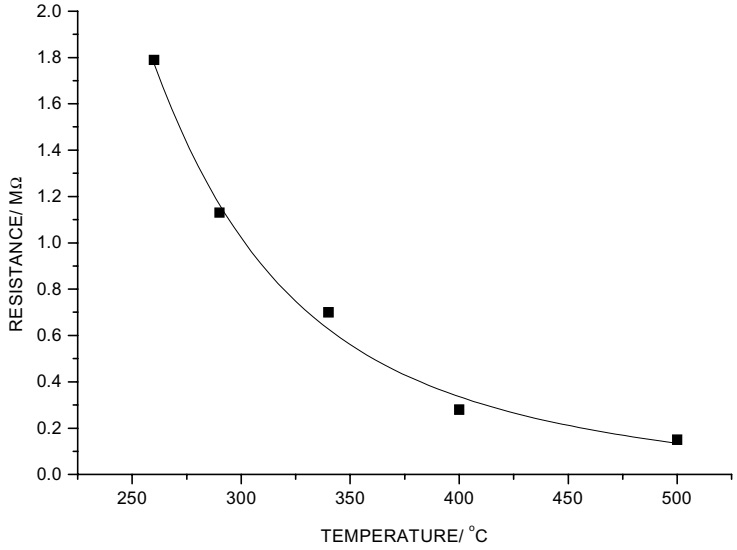

Figure 1. The resistance-temperature curve of Ag^- doped CuO-$BaTiO_3$ sensor.

Fig. 2 shows the dependence of the sensor sensitivity on temperature. The concentration of CO_2 for this test has been maintained at 5000 ppm. It's seen that the sensitivity of the sensor to CO_2 depends significantly on operating temperature. The sensitivity decreases both when temperature is too high and when temperature is too low. When the temperature is <350^{o}C, the material isn't active enough so the sensitivity is very low; When the temperature is >500^{o}C, the resistance of the material decreases and the influence of CO_2 on the sensor's conductance becomes relatively less, and the absorption coefficient of CO_2 decreases as well. Therefore, the sensitivity decreases when the operating temperature is too high.

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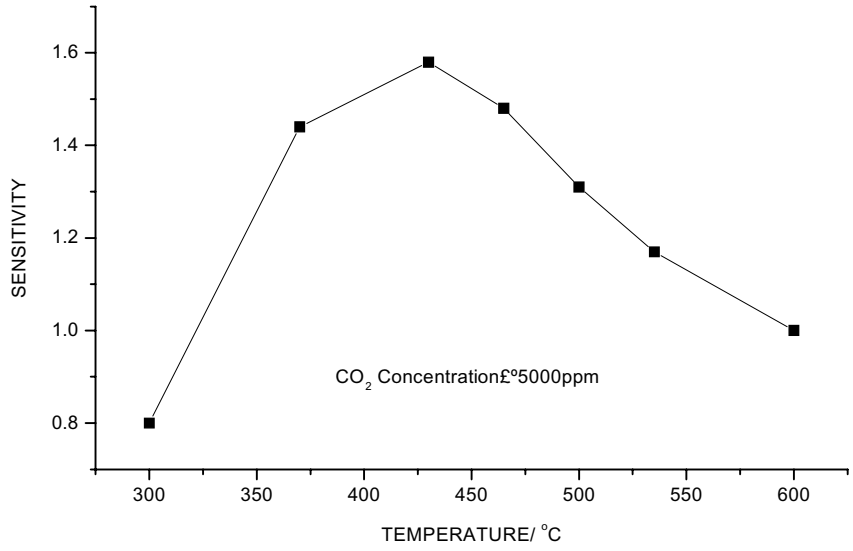

Figure 2. The temperature-sensitivity curve of Ag^{-} doped CuO-$BaTiO_3$ sensor.

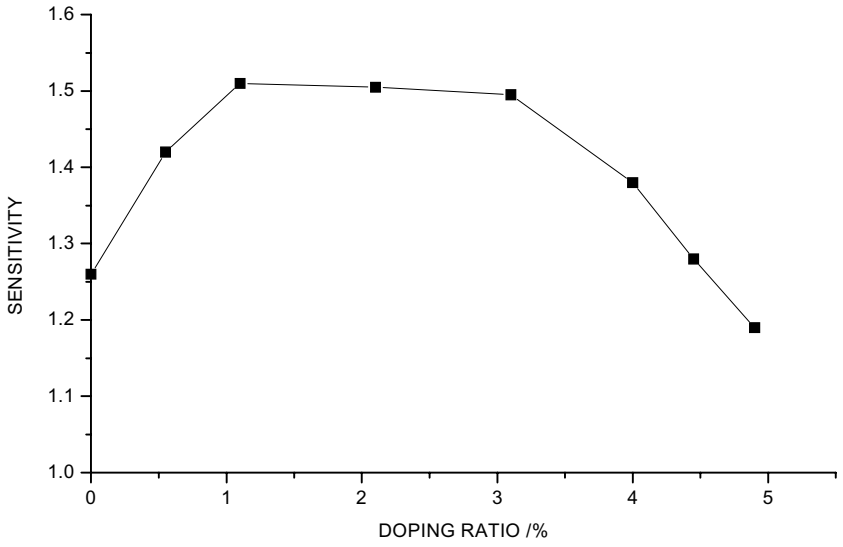

Figure 3. Dependence of sensor sensitivity to CO_2 on Ag- doping ratio.

Influence of Ag^{--}Doping on CO_2 Sensitivity

The doping ratio of Ag element influences not only the sensitivity and operating temperature, but also the resistance of the sensor in clean air. Fig. 3 shows the relationship between resistance and Ag doping ratio. As the doping ratio increases, the sensitivity of the sensor to CO_2 increases. When the ratio increases to 1%mol, the sensitivity reaches a plateau, and remains almost constant in the doping

range of 1%-3%. When the Ag doping ratio exceeds 3%mol, the sensitivity begins to decrease slowly. The sensor shows no sensitivity to CO_2 when Ag doping ratio exceeds 6%.

Fig. 4 shows the relationship between Ag doping ratio and sensitivity of the sensor to CO_2. As is seen the resistance of the doped material decreases with increasing Ag-doping ratio because Ag ionizes and affects conductance of the material. When the Ag- doping ratio reaches a certain value, however, the conductance of ionized Ag is dominant and the sensor's resistance decreases to such a low value that it is no longer sensitive to the presence of CO_2 gas. Based on this characteristic we can adjust the resistance of the sensor by changing the Ag- doping ratio in order to meet different design requirements.

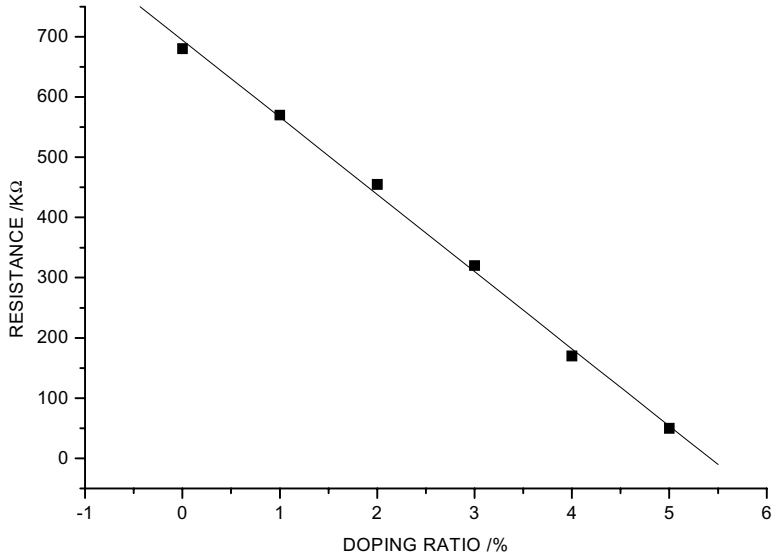

Figure 4. Relationship between Ag doping ratio and sensor's resistance.

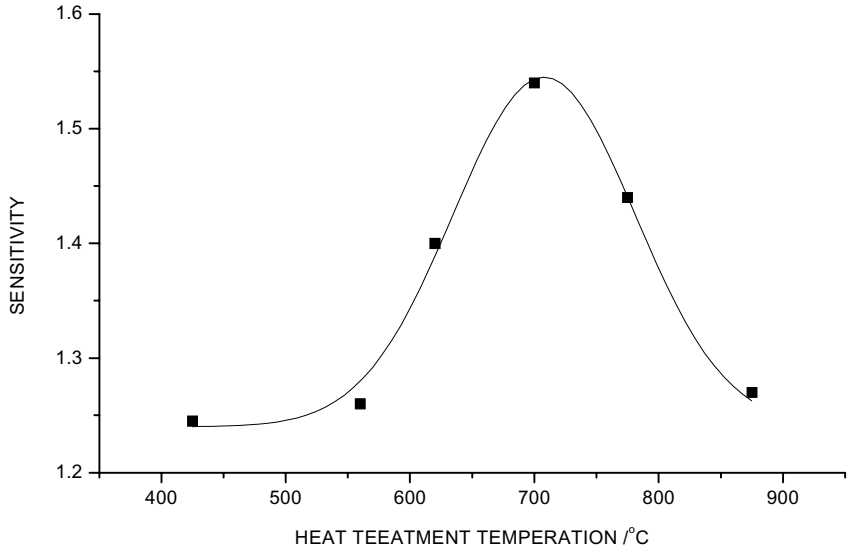

Figure 5. Relationship between sensor's sensitivity and sintering temperature.

Influence of Sintering Temperature on CO_2 Sensitivity

As is shown in Fig. 5, the sensitivity of the CuO-$BaTiO_3$ based sensor to CO_2 is affected significantly by the sintering temperature. The sintering time is 4 hours. The sensitivity is measured in 5000 ppm CO_2 at 430^{o}C operating temperature. As can be seen from fig. 5 the highest sensitivity is obtained when sintered at 700^{o}C. Too low a sintering temperature or too short a sintering time is disadvantageous to the decomposing and separation of $AgNO_3$. Besides, the material is not stable in structure. When the sintering temperature is too high, the BET value decreases, and so does the absorption of CO_2 gas. These result in decreases in the sensitivity of the sensor.

C-S Characteristics of Ag^- Doped CuO-$BaTiO_3$ Sensor

The sensor's response increases with increasing concentration of CO_2, as is shown in Fig.6. Note the concentration coordinate in the Fig.6 is in logarithm. The Ag- doped CuO-$BaTiO_3$ sensor has a lowest detection limit of 100 ppm of CO_2. Above 500 ppm the sensor has very good response. Since the sensor is not saturated until the concentration of CO_2 reaches 10%, the detection range for this sensor is from 100ppm to 10% CO_2.

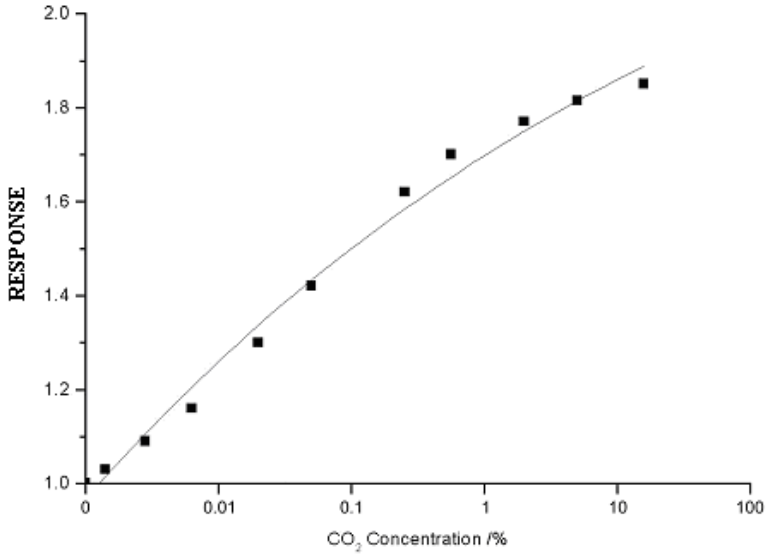

Figure 6. Sensitivity vs. concentration of CO_2 of the CuO-$BaTiO_3$ based sensor.

The sensitivity of the sensor to CO_2 gas is dependent on the electrode material used in the sensor. By testing Ag, Pt, Au as electrode materials, it was observed that the sensor with Ag electrodes has the highest sensitivity to CO_2, which attributes to the fact that Ag increases the CO_2 absorption on the surface just as the effect of doping Ag in the material. Ag acts as a catalyst. It adsorbs CO_2 gas molecules to produce silver carbonate, which then reacts with CuO-$BaTiO_3$ and makes the sensor more sensitive to CO_2.

Selectivity of Ag^- Doped CuO-BaTiO3 Sensor

Fig 7 shows the sensitivities of the sensor to several common gases. Compared with the sensitivity

to CO_2, the sensitivities to other gases are very low (except CO), indicating the CuO-$BaTiO_3$ based gas sensor has good selectivity to CO_2. The sensor is sensitive to CO gas because CO is easy to oxidize to CO_2 at such a high temperature and especially with Ag's catalyzing effect. Nevertheless, the sensitivity to CO is much lower than that to CO_2, as is seen from Fig. 7.

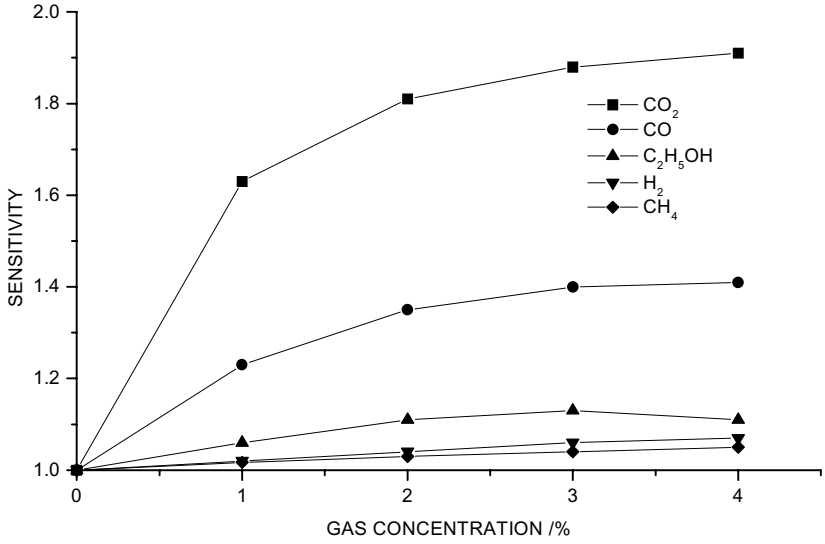

Figure 7. Selective characteristic of CuO-$BaTiO_3$ based CO_2 sensor.

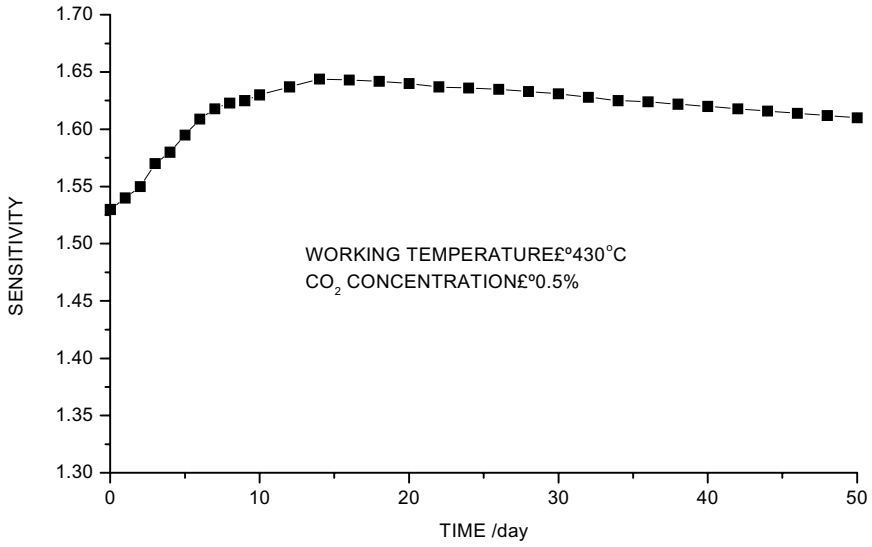

Figure 8. Stability of CuO-$BaTiO_3$ based CO_2 sensor over time.

Stability of the CuO-BaTiO3 Based CO_2 Sensors

The sensitivity of the sensor to CO_2 was recorded as a function of time. As is shown in Fig. 8, the sensitivity rises in the first 10 days, and then remains relatively stable. The initial increase in sensitivity is believed to be caused by activation and redistribution of the adulterated impurities.

Repeating absorption and desorption processes and redistribution of Ag in the material improve the activation and enhance the absorption and reaction of CO_2, causing gradual increases in the sensitivity. The sensitivity becomes more stable after this "conditioning" process is completed.

Conclusion

CuO-$BaTiO_3$ based CO_2 sensor has been studies. The sensor has increased sensitivities to CO_2 when doped with elemental metals, with the working temperature increases as well. Among the metal elements tested, Ag- doped CuO-$BaTiO_3$ sensor has high sensitivity and low working temperature. The Ag-doped sensor has a detection concentration range of 100 ppm to 10% CO_2. Compared with other types of CO_2 sensor such as potentiometric or SAW sensor, the working temperature of the semiconductor CO_2 sensor is slightly higher, and the sensitivity still needs to be improved.

Acknowledgements

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Sample Availability: Available from the authors.