PREPARATION OF CAPACITIVE-TYPE CO_2 GAS-SENSITIVE ELEMENT USING NANOMETER POWDERS①

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ABSTRACT Nanometer $BaTiO_3$ and CuO powders were prepared by means of mechanophysical solid phase effects and powder metallurgy technology. A capacitive-type gas-sensitive element was made from those two powders, the results of gas-sensitive characteristics indicate that the element has good sensitivity to CO_2 gas. XRD and SEM analyses show that the element is just a homogeneous functional composite which is made from two phases by simply mechanical mixing.

Key words nanometer powder CuO-$BaTiO_3$ capacitive element gas-sensitive characteristic

1 INTRODUCTION

Recently, a great attention has been paid to the development and application of environmental gas sensors[1-3]. The researches on solid electrolyte sensor are rather active[4-6], CO_2 was determined by the voltage difference between gas CO_2 and the alkaline carbonate coated on working electrode, but the structure of sensor is complicated, and the alkaline carbonate is deliquescent and stongly affected by water vapor, therefore the requirement for preparation of electrode is very strict[1]. Because the chemical property of CO_2 is stable, it was thought that the metal oxide semiconductor-type sensor could not be used for determining CO_2, but a research[2] reported SnO_2 which added alkaline oxide is sensitive to CO_2 in some degree, while its preference to CO_2 is bad and the stability isn't ideal. The main determination methods above mentioned adopted signal processing related to direct current determination. In 1990, Ishihara first found that P-N compound oxide is sensitive to CO_2 gas, and produced a new semiconductor capacitive-type sensor[7]. Compared with other sensors, the structure is simple, sensitivity and selectivity are good, determination range is rather wide, and also it is easy to be small-scaled and to be integrated, so it has a promising future. Meanwhile, the method adopts the signal processing related to alternating current determination, it can not easily be affected by testing environment, while it can be amplified easily and can get high SIN, therefore it is suitable for high sensitive analysis. Except for humidity sensor, there are few researches on the capacitance changing sensor[8]. The semiconductor capacitive-type CO_2 sensor was developed in this paper, the nano-and semiconductive theories were introduced into the element preparation, the mechanically mixed function composite with sensitive property to CO_2 gas was prepared.

2 EXPERIMENTAL

2.1 Nanometer and semiconductive $BaTiO_3$ powders preparation

The nanometer and semiconductivity $BaTiO_3$ powders were prepared by mechanophysical solid effects and powder metallurgy technology[9]. The prepared equal-mole $BaCO_3$ (99.89%) and TiO_2 (99.7%) nanometer powders were mixed and then put into the quartz tube which was put in silicon carbide rod furnace.

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The temperature was increased to 1 200 ℃ under a certain sintering regulation and kept for 12 h. After being air-cooled to room temperature, the $BaTiO_3$ powders were obtained.

2.2 Nanometer CuO powders preparation

The spectrum pure CuO (99.99%) powders was used as raw material, the ratio of the powder to ball was controlled to be 1∶8, and the rotating speed of ball grinder was 225 r/min. Nanometer CuO powders were prepared in Ar atmosphere through a mechanophysical solid effects apparatus.

2.3 Nanometer gas sensitive element preparation

The prepared nanometer semiconductive $BaTiO_3$ powders were used as main raw material, and a dulterated mechanically and evenly with a certain mole proportion of prepared nanometer CuO powders, then the mixed powders were pressed into disks (d 13 mm × 0.6 mm). After calcination at 773 K for 5 h, Ag paste was applied on both faces of the disks to make an electrode (6 mm in diameter), thus the sensitive element for determination was fabricated. The procedure similar to that of Ref. [7].

2.4 Basic sensitive property determination

The experimental apparatus suitable for CO_2 gas-sensitive element characteristic determination was developed and introduced by Ref. [10]. Sample gas (the concentration of CO_2 can be controlled randomly) came from the gas cylinder which was diluted by dry air. The stable CO_2 airstream of certain concentration was obtained through flowing stabilivalve, flow meter and mixture bottles. The channel of gas was divided into two parts, which was controlled by triple valve, the switching between CO_2 airstream and atmosphere one could be finished rapidly, the response time is within a few seconds, and dynamic characteristic of element could be reflected timely. The exhaust was absorbed by lye. The sensitivity is defined as the ratio of capacitance of the element in CO_2 sample gas to that in atmosphere, namely Cs/Co.

3 RESULTS AND DISCUSSION

3.1 Structure characteristic of $BaTiO_3$ powders

X-ray diffraction analysis of production (Fig. 1(a)) shows that there exist the (200), (020) and (002) diffraction double peaks when 2θ is about 45°, which can be defined as tetragonal $BaTiO_3$ structure without other impure phases. TEM results (Fig. 2) indicate that the crystals in a cluster are well-distributed, and the size range is 40~60 nm.

3.2 Structure characteristic of CuO powders

The phase composition of CuO powders was determined by D-500 X-ray diffractometer, the morphology of powders was observed by Hitach H-800 TEM, as shown in Fig. 1(b) and Fig. 3. The results indicate that the main crystal phases of powders are monoclinic CuO, and the size range is 15~20 nm.

3.3 Sensitive characteristic of gas-sensitive element determination

The temperature was set to be 542 K and the element was put in atmosphere airstream, after stabilization for a certain time while the frequency is fixed to be 50 kHz, its capacitance was determined. Then the airstream was switched rapidly to CO_2 gas, the response characteristic of sensitivity of element to 2% CO_2 was studied, the results were shown in Fig. 4.

It is known from Fig. 4, the value of capacitance of the element changes rapidly when time is over 10 s, but the value tends to be constant needs 120 s or more. When the capacitance of the element reached stable-state, switched the CO_2 airstream to atmosphere, then determined the capacitance of the element at each fixed time. The obtained recovering characteristic curve of sensitivity of the element was plotted in Fig. 5. It is known from Fig. 5, the valve of capacitance of the element approached its original value 300 s later. The recovering charactersitic of sensitivity response indicates that the obtained element has good sensitivity to CO_2 gas.

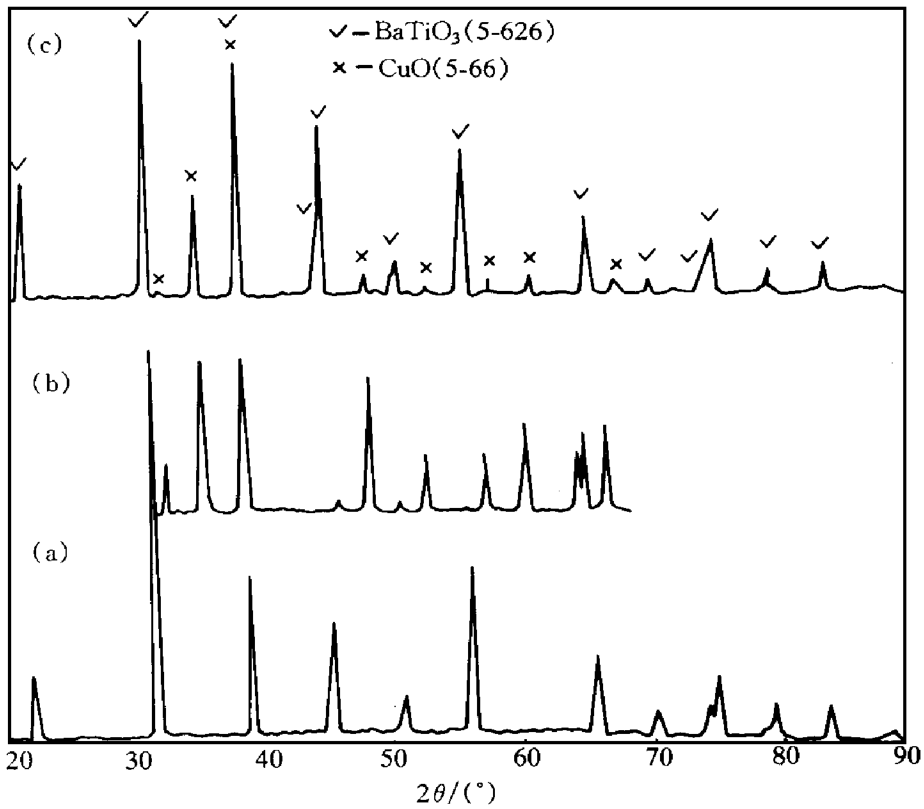

Fig. 1 X-ray diffraction patterns of nanometer powders
(a) —X-ray diffraction pattern of nanometer $BaTiO_3$;
(b) —X-ray diffraction pattern of nanometer CuO;
(c) —X-ray diffraction pattern of gas-sensitive element

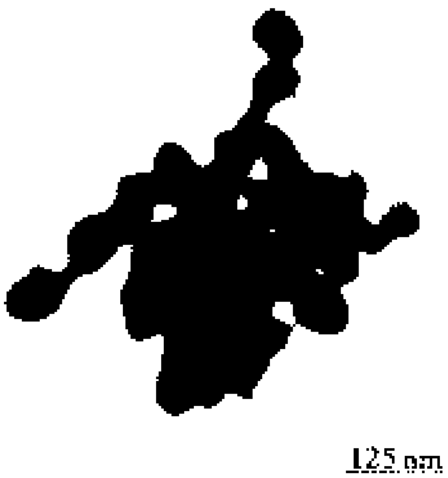

Fig. 2 TEM morphology of nanometer $BaTiO_3$ powders

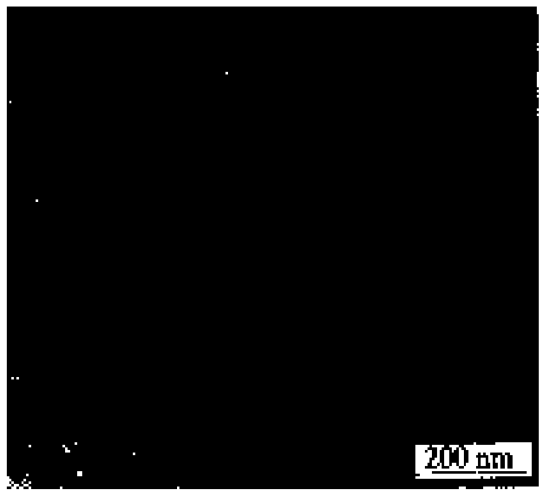

Fig. 3 TEM morphology of nanometer CuO powders

It is known from the result of XRD of element (Fig. 1(c)) that there exists no solid phase reaction between CuO and $BaTiO_3$ at temperatures below 500 ℃, just mechanical mixture. The morphology of element was observed by JSM-35C SEM, as shown in Fig. 6, the crystals and gas holes are well-distributed, which is benifical to the absorption of gas.

4 CONCLUSIONS

(1) Tetragonal nanometer $BaTiO_3$ powders can be obtained by mechanophysical solid phase

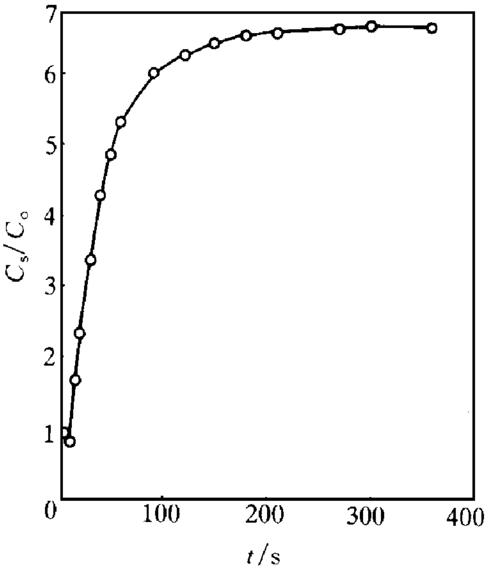

Fig. 4 Response characteristic curve of sensitivity of element

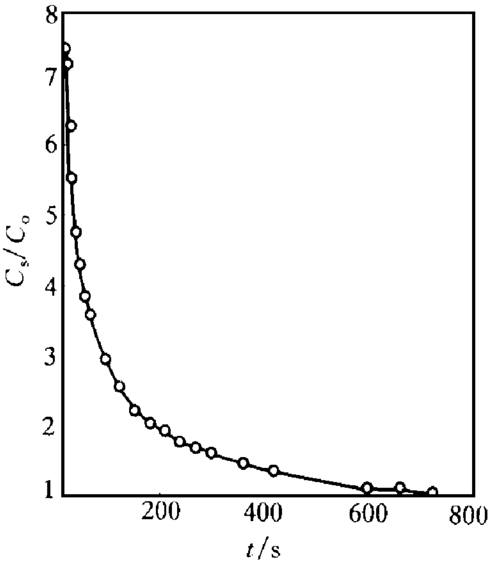

Fig. 5 Recovering characteristic curve of sensitivity of element

effects and powder metallurgy technology. The powders are well-crystallized and distributed in a cluster and have a narrow size range as well.

(2) Nanometer CuO powders are prepared by mechanophysical solid phase effects. The powders are also well crystallized and distributed.

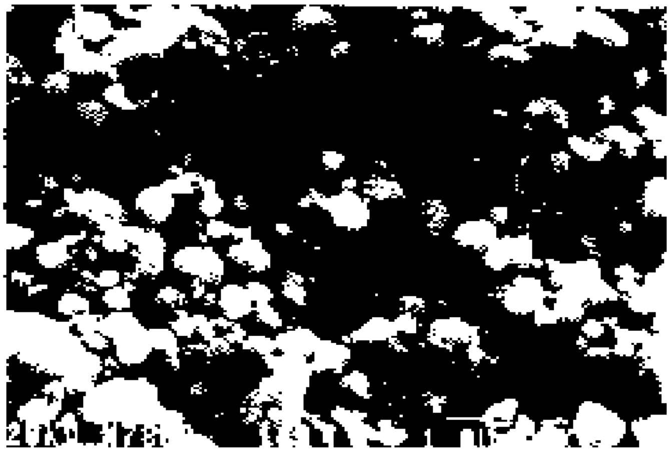

Fig. 6 SEM morphology of gas-sensitive element

(3) Nanometer CuO-BatiO$_3$ capacitive gas-sensitive element are developed, and the results indicate that the element has good sensitivity to CO_2 gas.

(4) XRD and SEM analyses indicate that there exists no solid phase reaction between the two phases of element, but only the simply mechanical mixture of raw powder materials.

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