Microelectronic Engineering 86 (2009) 2320–2323

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Low temperature sintering properties of Y-doped $BaTiO_3$ ceramics by BaB_2O_4 sintering aid

Myongil Kong *, Shenglin Jiang, Tiantian Xie, Haibo Zhang

Department of Electronic Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 8 August 2007
Accepted 10 April 2009
Available online 18 May 2009

Keywords:
BaB_2O_4
Low temperature sintering
Y-doped $BaTiO_3$ ceramics

ABSTRACT

The sintering process of semiconducting Y-doped $BaTiO_3$ ceramics added with BaB_2O_4 as low temperature sintering aid were investigated. When the low temperature sintering aid BaB_2O_4 added Y-doped $BaTiO_3$ ceramics prepared by Sol–Gel method, the sintering temperature of $BaTiO_3$-based ceramics would be greatly decreased, and also widen sintering range. Y-doped $BaTiO_3$ ceramics with BaB_2O_4 addition can be obtained at 1050 °C. Ceramics samples with room temperature resistivity 60–80 Ω cm, ratio of the maximum resistivity to minimum resistance (Rmax/Rmin) 10^4 and temperature coefficient of resistivity (α) 10%/°C were obtained.

1. Introduction

Since its discovery in 1954, semiconducting $BaTiO_3$ ceramics has been extensively used in various fields; electronic information, automatic control, biological technology, energy management and traffic control as important control component, due to its particular properties.

At the present time, the PTC thermistors based on $BaTiO_3$ semiconducting ceramic materials become the important application aspects in ferroelectrical ceramic application. However, as conventional PTCR ceramics have high sintering temperature (1300 °C or higher), it is rather difficult to fabricate multilayer PTCR devices with ohmic contacts between the ceramic and the electrode by a co-firing process. Therefore, an effort to lower the sintering temperature of PTCR ceramics is an important research field. Normally, an eutectic mixture of $Al_2O_3 \cdot SiO_2 \cdot TiO_2$ (AST) is commonly added as a sintering aid to form a liquid phase at a relatively lower temperature during sintering so as to control the microstructural development and to improve the PTCR effect. Without them, semiconducting $BaTiO_3$ ceramics generally have high room temperature resistance or even become insulators. But the sintering temperature of semiconducting $BaTiO_3$ ceramics with AST is still higher than 1200 °C [1]. Therefore it is important problem to lower the sintering temperature even more by using some other sintering aids. LiF, Li_2O as the sintering aid lower the sintering temperature to below 1000 °C [2], but the incorporation of Li makes the n-doped $BaTiO_3$ become an insulator due to the acceptor type characteristics of Li [3,4]. Liquid-phase sintering of $BaTiO_3$ through the addition of B has been report. Since B_2O_3 has a very low melting point (about 450 °C), it volatizes and makes $BaTiO_3$ porous after sintering [5].

Therefore BN, which oxidizes at temperatures above 1000 °C in air, is used as the B source. BN addition is effective sintering aid in the PTCR device [6,7]. In this paper, when the low temperature sintering aid BaB_2O_4 added Y-doped $BaTiO_3$ ceramics prepared by Sol–Gel method, properties of the low temperature sintered $BaTiO_3$ and its PTCR characteristics were investigated.

2. Experimental procedure

Samples were prepared by the Sol–Gel technique. Barium acetate ($Ba(CH_3COO_2)_2$), strontium acetate ($Sr(CH_3COO_2)_2$) and titanium tetrabutoxide ($Ti(C_4H_9O)_4$) are used as the starting material. Powder of $Y(NO_3)_2$ was added to impart the semiconducting properties. To improve sintering, BaB_2O_4 was added as low temperature sintering aid. The amounts of materials used were based on the following formula: $(Ba_{0.75}\ Sr_{0.25}\ Y_{0.006})Ti_{1.02}O_3$. At first, Barium acetate, strontium acetate and powder of $Y(NO_3)_2$ were dissolved in appropriate amounts of distilled water, and agitated until the solution become transparent. On the other hand titanium tetrabutoxide is mixed in appropriate amount of ethyl alcohol and acetic acid (A.R. grade) was used to keep PH of the above solution at about 5.0. After that, the first solution is added slowly to the titanium tetrabutoxide solution and stirred in a magnetic stirrer for about 2 h at room temperature to form transparent and homogenous sol of Ba–Sr–Y–Ti. The sol transformed into gel by hydrolysis effect. The wet gels obtained were dried at 100 °C for 24 h and finally annealed at 800 °C for 2 h. BaB_2O_4 as sintering aids

* Corresponding author.
E-mail address: xttyh@163.com (M. Kong).

0167-9317/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.mee.2009.04.029

were used 0.1–1 mol% $BaCO_3$ and 0.5–1.5 mol% H_3BO_3 with purities higher than 98wt%. After mixed uniformly, the materials were put into a platinum crucible and melted by an electric furnace at 1000 °C for 30 min. The molten glass was quenched into distilled water to form cullet. The cullet was dried and milled by ball milling for 10 h. These two kinds of powers (Y-$BaTiO_3$, BaB_2O_4) were mixed together and ground by ball milling for 24 h to obtain fine powers. The powers prepared above were mixed with 8 wt.% of 10% PVA solution and then pressed into disc-shaped pellets. The green pellets were sintered at a temperature range of 900–1250 °C for 1–3 h in air and then furnace-cooled.

To investigate the sintering behavior, the microstructure of the sintered samples was observed using electron microscope (SEM-Leica Stereoscan 440). Densification behavior of samples was observed with the shrinkage (dL/Lo) of the diameter direction. Electrodes were prepared by using ohmic Al pastes on both surfaces of the ceramic disk samples. The electrical resistivity was measured as a function of temperature using a digital multi-meter in a temperature-programmable tube furnace at a heating rate of 2 °C min^{-1}.

3. Results and discussion

Fig. 1 shows the shrinkage (dL/Lo) as a function of the sintering temperature for Y-doped $BaTiO_3$ with 1, 3 and 6 mol% of BaB_2O_4. The densification rate at low sintering temperature depends on the amount of BaB_2O_4 added. However all the samples have the close density when the sintering temperature reaches around 1000 °C. BaB_2O_4 promotes the densification process probably by reacting with $BaTiO_3$ to create a liquid phase at relatively low temperature during sintering. The influence of the amount of BaB_2O_4 and sintering temperature on the room temperature resistivity of Y-doped $BaTiO_3$ ceramics illustrated in Fig. 2. It can be seen that room temperature resistivity decreases with increasing sintering temperature. At high sintering temperature, less amount of BaB_2O_4 is lowed room temperature resistivity. In contrast, at low sintering temperature, increase in the amount of BaB_2O_4 is also lowed room temperature resistivity. In the case of 3 mol% BaB_2O_4 added specimen, the lowest value of room temperature resistivity was found. The decrease of room temperature resistivity with BaB_2O_4 addition seemed to originate from a decrease of porosity with acceleration of densification in specimens.

The microstructures of the sample with 1 mol% BaB_2O_4 sintered at different temperature are shown in Fig. 3.

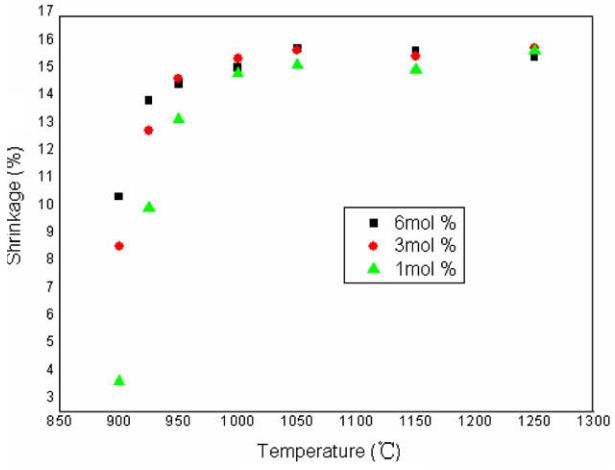

Fig. 1. Shrinkage of Y-doped $BaTiO_3$ ceramics with different amounts of BaB_2O_4.

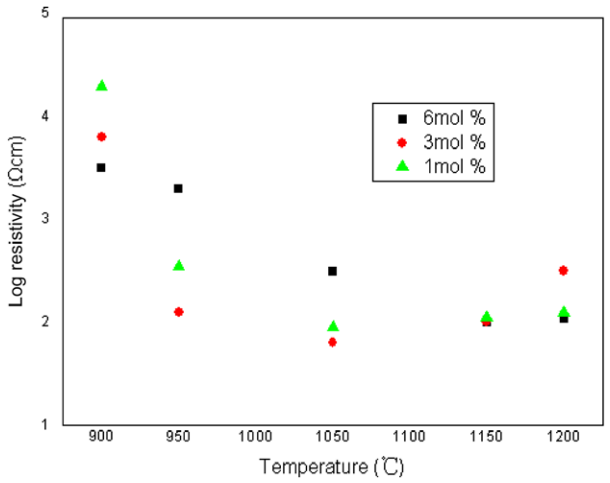

Fig. 2. Room temperature resistivity of Y-doped $BaTiO_3$ ceramics with different amounts of BaB_2O_4.

In Fig. 3a, the sintering temperature of 900 °C is too low to produce complete sintered bodies. The sintering temperature of 925 °C is still low, as shown in Fig. 3b. Grain boundaries can be seen, and there are pores between dense areas. Sample sintered at 925 °C shows the intermediate microstructure of the sample sintered at 900 °C and 950 °C. This may be the cause of the higher room temperature resistivity. With increasing the sintering temperature, the size of the grains increases, and room temperature resistivity drops sharply. When the sintering temperature is augmented to 1050 °C, the uniform grain growth (Fig. 3d) is enhanced so that a significant reduction in room temperature resistivity can be seen. The further increase in the sintering temperature (1150 °C) only leads to a slight change in the grain size and the room temperature resistivity. But at sintering temperature above 1200 °C, there are many fine grains in the samples although the sample is well densified and hence suppression of anomalous grain growth and a large number of grain boundaries. As shown in Fig. 3f, a few pores present are located mainly at the grain boundaries and occasionally inside the grains. Prolonged sintering above 1200 °C resulted mostly in an excessive weight loss due to volatilization, and hence its room temperature resistivity increased. Therefore, the influence of BaB_2O_4 addition on room temperature resistivity is related to its effects on the microstructure. In the presence of BaB_2O_4, the sintering process can be a liquid-phase sintering in terms of dissolution and precipitation of materials. The formation of microstructure depends strongly on the amount of liquid phase. Because the glass phases and the Y-doped $BaTiO_3$ phases are homogeneously mixed, the glass-ceramic samples can be sintered well at much lower temperature. Increase in BaB_2O_4 amount and sintering temperature is favorable for generation of more liquid phase facilitating uniform microstructural development, which results in a low room temperature resistivity.

In Fig. 4, the microstructures of the sample with 1 mol% BaB_2O_4 sintered at different sintering time are shown.

As shown in Fig. 4, the sintering characteristics of Y-doped $BaTiO_3$ ceramics with 1 mol% BaB_2O_4 addition were found to vary with sintering time. In general, a significant enhancement of densification was observed when samples were sintered at temperature above 800 °C, which is the melt formation temperature in the system. This suggests that the sintering kinetics are probably controlled by the formation of a liquid phase. When sintering at 950 °C for 1 h (Fig. 4a), the microstructure is not likely to be developed as a consequence of continuous grain growth because of the presence of a small amount of liquid phase. The density of the sin-