行政院國家科學委員會補助專題研究計畫成果報告

ZnO 變阻陶瓷毫米波燒結技術研究(II)
(Mini-meter Wave Sintering of ZnO)

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1. Introduction

Zinc oxide ceramics with several additives are employed as varistor materials because of their highly nonohmic behavior in current-voltage (I-V) characteristics and excellent surge withstanding capability\(^1\). These ZnO-based varistors are, therefore, extensively employed as transient surge suppressors against dangerous abnormal high voltages in protecting electronic circuits\(^5\). It is believed that nonlinear voltage-current characteristics of these materials resulted from the grain boundary layer, which is essentially formed by a segregation of large ionic additives such as Bi\(_2\)O\(_3\), Pr\(_2\)O\(_3\), and BaO at the grain boundary.\(^7\) These “varistor-forming” ingredients not only affect the electrical properties but also the densification behavior and microstructure evolution of ZnO ceramics.

It is generally accepted that the microwave sintering process can densify the ceramic materials in a very rapid rate and at a substantially lower temperature\(^1\). Therefore, this technique was adopted in this work to prepare the ZnO-Bi\(_2\)O\(_3\) materials. Moreover, the materials absorbed microwave power per unit volume is given by\(^1\)

\[
P = 2\pi f \epsilon_0 |\mathbf{E}|^2 / 2
\]

where \(f\) is the microwave frequency, \(\epsilon_0\) is the permittivity of free space, \(\mathbf{E}^*\) is the imaginary part of the complex dielectric constant of the dielectric constant and \(E\) is the microwave electric field in the material.

Therefore, the materials absorbed microwave power more efficiently at higher frequency\(^1\).

In this work, we have made an extensive examination on the effect of heating rate and microwave frequency on the densification behavior of this ZnO-Bi\(_2\)O\(_3\) based ceramics, emphasizing the correlation between the microstructure characteristics of the materials with their voltage-current (V-I) and capacitance-voltage (C-V) behavior.

2. Experimental Procedure

The ZnO samples were prepared from a commercial high-purity (>0.999) zinc oxide powder, containing 3 mol% Bi\(_2\)O\(_3\) and a little amount of Mn\(_2\)O\(_3\), CoO, NiO, Nb\(_2\)O\(_5\) and Na-glass as microstructure stabilizers and nonlinear properties promoters. The samples were uniaxially pressed at 750 kgf/cm\(^2\) into a disk of 16 mm in diameter and 2 mm in thickness. The green pellets, around 61% of theoretical density (TD) were microwave sintered at 1100 °C (0 min soaking time) in an applicator, with the heating rate varied. The 2.45 GHz microwave generated from a magnetron (CEM, MAS-700, 1 kW) or the 24 GHz millimeter-wave generated from a Gyrotron (MICRAMICS INC, 5 kW) were used. The sample holder was a hollow cylinder made of alumina-silica fiberboard, which contains 5 SiC rods placed at inner wall as a susceptor. The temperature profile was measured using Pt 13% Rh thermocouple placed near the sample surface. The samples were heated in a rate of 30 °C/min, 60 °C/min or 120 °C/min for a sintering temperature above 500 °C and then cooled in a rate of 145 °C/min as soon as the sintering temperature reaches 1100 °C, with 0 min soaking time, for comparison, the samples were also densified by a conventional sintering process, that is, sintering in an electrical furnace at 1100 °C -0 min with 30 °C/min heating rate.

The crystal structure and microstructure of the sintering samples were examined using Rigaku D/mas-
□ B X-ray diffractometer (XRD) and Hitachi S3500 scanning electron microscope (SEM), respectively. The density of sintered specimens was measured by the Archimedes method. The average grain size, G, were calculated as described by Mendelson18 with a multiple factor of 1.56 the voltage-current (V-I) properties of these samples were recorded using Keithley 237 I-V electrometer in dc source after the silver paste was rubbed onto the sample surface and fired at 600 ºC for 10 min to serve as electrodes. Breakdown voltage (V_{bd}) was measured at current density of 1 mA/cm², nonlinear coefficient (β) was estimated for a current density ranges from 0.5 mA/cm² to 5 mA/cm² and leakage current density (I_{leak}) was defined as the current density at 0.8 V_{bd}. The capacitance–voltage (C-V) measurements were made at room temperature using HP4272A capacitance meter. The electrical characteristics, including barrier height (φ_b) and donor density (N_d), were determined from capacitance-voltage (C-V) data, using the model proposed by K.Mulae(18). The surface state density (N_s) was calculated from φ_b and N_d, using the relationship

\[ N_s = (2Nd\varepsilon_o \sqrt{\varepsilon_o / q})^{1/2} \]  

Where \( \varepsilon_o \) is the dielectric constant of ZnO, \( \varepsilon_o \) is the permittivity of vacuum, q is the electron charge.

3. Results

3.1 General characteristics

The phase constituents of the microwave (millimeter wave) sintered ZnO materials are shown as X-ray diffraction pattern in Fig. 1, indicating that they contain hexagonal ZnO as the main constituents, with Bi-rich (Bi₄ₓZnO₃₋₁ₓ) and spinel as secondary phase. Similar kind of phase structure was also observed for the ZnO materials densified by the conventional furnace sintering process. The ZnO materials can not be fully densified by fast firing process using a conventional sintering (cS) technique. The sample can only reach 88.3 % TD (theoretically density), when sintered at 1100 ºC-0 min with 30 ºC/min heating rate (open diamonds, Fig. 2a). It usually needs higher sintering temperature, longer soaking time (1200 ºC, 60 min) and slower temperature ramping rate (5 ºC/min) to achieve a sintered density as high as 96% TD. By contrast, the materials can be effectively densified, by using either microwave (2.45 GHz) or millimeter-wave (24 GHz) sintering process, which implies that densification rate is markedly enhanced in these process. The sintered density attainable for millimeter-wave (ms) ZnO materials is around 93% TD (open circles, Fig. 2a), where that for microwave sintered (µs) samples is only around 93% TD (open squares, Fig 2a), when the heating rate was controlled at 30 ºC/min. The sintered density is smaller for the samples heated in faster rate.

Figure 1 X-ray diffraction patterns (Cu Kα) of ZnO materials densified by (a) 2.45GHz microwave sintering (µS) process at 1100 ºC (30 ºC/min), (b) 24GHz millimeter-wave sintering (mS) process at 1100 ºC (30 ºC/min) and (c) conventionally furnace sintering (cs) at 1100 ºC (30 ºC/min).

Figure 2 The variation of (a) relative density and (b) average grain size of Bi₂O₃–based ZnO materials, densified by microwave (2.45 GHz) or millimeter-wave (2.45 GHz) sintering process, with 30 ºC/min, 60 ºC/min or 120 ºC/min heating rate.

3.2 SEM morphology

The ms- and µS-process also impose pronounced enhancement on the grain growth behavior of the ZnO materials. As shown in the SEM microstructure (Fig. 3) for the samples sintered at 1100 ºC-0 min, the grains hardly grow when conventionally sintered and has grown to around 3 µm when microwave sintered, which is still smaller than the grain size obtained for the millimeter wave sintered samples (~6.8 µm). The grain size decreases for the samples sintered using a faster ramping rate, which are plotted in Fig. 2b. These results reveal that only enhances the densification kinetics for the ZnO materials but also increases their grain growth rate.

3.3 The electrical properties

The electrical properties of the Bi₂O₃-based ZnO materials wave characterized by their electric field-current density (E-J) and capacitance-voltage (C-V) properties, which are shown as Fig. 4 and 5, respectively. The samples conventionally sintered at 1100 ºC (0 min) are too lately to exhibit good enough nonlinear properties (dotted curve, Fig. 4a), which is
attributed to low sintered density and small grain microstructure of the corresponding samples. It needs 1200 °C-60 min (with 5 °C/min ramping rate) to densify the ZnO materials and induce the grain growth, so as to attain large nonlinearity in electrical properties (solid curve, Fig. 4a), which is attributed to low sintered density and small grain microstructure of the corresponding samples. It needs 1200 °C-60 min (with 5 °C/min ramping rate) to densify the ZnO materials and to induce the grain growth, so as to attain large nonlinearity in electrical properties (solid curve, Fig. 4a).

Figure 3 SEM micrographs of Bi₂O₃ based ZnO materials densified at 1100 °C by (a) conventional furnace sintering (30 °C/min) and (b) 2.45 GHz microwave sintering (30 °C/min) and (c) 24GHz millimeter-wave sintering, which 30 °C/min heating rate.

All the samples densified by millimeter-wave or microwave sintering process exhibit good nonlinear properties. The varistor parameters were derived from the E-J curves and are shown in Fig. 5a, 5b and 5c for nonlinear coefficient (α), leakage current density (Jₐ) and breakdown voltage (Vₗ₈), respectively. The nonlinear coefficient (α) for the mS-(or μS-) samples increases with the ramping rate used for sintering, and the α-values of the millimeter-wave sintered materials are much higher than that of the microwave sintered materials for all sintered conditions. The leakage current density (Jₐ) is smaller and the breakdown voltage (Vₗ₈) is larger for samples sintered by a faster heating rate, which is associated with the smaller grain size of the materials.

Figure 4 The electrical field-leakage current(E-J) properties of ZnO samples (a) conventionally sintered at 1100 °C-0 min (30 °C/min) or 1200-60 min (5 °C/min), (b) 2.45 GHz microwave sintered and (c) 24 GHz millimeter-wave sintered at 1100 °C-0 min with 30 °C/min, 60 °C/min or 120 °C/min heating rate.
Figure 5. The variation of (a) nonlinear coefficient, $\alpha$, (b) leakage current density, $J_L$, and (c) breakage voltage, $V_{bk}$, of ZnO samples sintered at 1100 °C-0 min with 30 °C/min heating rate, by using microwave (2.45GHz) or millimeter-wave (24 GHz) sintering process.

4. Conclusion

In this work, we observed that the BiO$_3$-based ZnO materials can easily be densified by millimeter-wave, microwave or conventional sintering process. The millimeter-wave sintering process can enhance the densification rate of the ZnO materials in a greater extent than the microwave sintering process. However, sintering at 1100 °C for too long period by millimeter-wave sintering process results in substantial decrease in nonlinear coefficient ($\alpha$), pronounced increase in leakage current density ($J_L$) and marked reduction in breakdown voltage ($V_{bk}$), which were accounted for too short temperature by microwave sintering process far too short period leads to insufficient in corporation of donors and surface states, which also results in low $\alpha$- and leakage $J_L$- values, but with high $V_{bk}$- values for ZnO samples.

5. References