

行政院國家科學委員會專題研究計畫成果報告

ZnO 變阻陶瓷毫米波燒結技術之研究(一)

(A Study on Mini-meter Wave Sintering of ZnO Varistor Ceramics(一))

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主持人: 郭正次 交通大學材料工程系

Fast firing of Bi₂O₃-based ZnO varistor materials, which includes zero minutes soaking at 1100°C with 120°C/min heating and 145°C/min cooling rate, was made possible by using millimeter-wave sintering (mS) technique. The overall sintering time of the process is less than 18 minutes, and the varistor characteristics obtained are $\alpha=38$, $J_L=5.55 \times 10^{-6}$ A/cm² and $V_{bk}=600$ V/mm, whereas the intrinsic parameters of the materials are $\phi_b = 2.84$ eV, $N_d = 1.85 \times 10^{24}$ m⁻³ and $N_i = 7.02 \times 10^{11}$ cm⁻². By contrast, conventional sintering (cS) process needs higher sintering temperature (1200°C), longer soaking time (60 min) and slower ramping rate (30°C/min) to obtain ZnO materials with the same marvelous nonlinear properties as those prepared by mS-process. Moreover, millimeter-wave sintering (24 GHz, mS) process enhances the densification kinetics and grain growth behavior more efficiently than the microwave sintering (2.45 GHz, μ S) process, resulting in better varistor characteristics for ZnO materials. However, sintering by millimeter-wave for too long period induces overfiring of the samples, which results in a density reversion phenomenon. Such a phenomenon leads to the decrease in surface state (N_i) and the potential barrier height (ϕ_b), which are presumed to be the mechanism leading to the degradation of ZnO materials' nonlinear properties.

KEYWORD : ZnO varistor, millimeter-wave sintering, microwave sintering, fast sintering.

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.⁽¹⁻⁴⁾ These ZnO-based varistors are, therefore, extensively employed as transient surge suppressers against dangerous abnormal high voltages surge for protecting electronic circuits.^(5,6) 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 Bi₂O₃, Pr₆O₁₁ and BaO at the grain boundary.⁽⁷⁻¹⁰⁾ 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.⁽¹¹⁻¹⁷⁾ Therefore, this technique was adopted in this work to prepared the ZnO-Bi₂O₃ materials. Moreover, the materials absorbed microwave power per unit volume is given by⁽¹¹⁾

$$P = 2\pi f \epsilon_0 \epsilon'' |E|^2 / 2 \quad (1)$$

where f is the microwave frequency, ϵ_0 is the permittivity of free space, ϵ'' is the imaginary part of the complex dielectric constant of the material and E is the microwave electric field in the material.

Therefore, the materials absorbed microwave power

more efficiently at higher frequency⁽¹⁷⁾.

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-Bi₂O₃ 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% Bi₂O₃ and a little amount of Mn₃O₄, CoO, NiO, Nb₂O₅ and Na-glass as microstructure stabilizers and nonlinear properties promoters. The samples were uniaxially pressed at 750 kgf/cm² 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 a 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-IIB 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°C for 10 min to serve as electrodes. Breakdown voltage (V_{bk}) was measured at current density of 1 mA/cm², nonlinear coefficient (α) was estimated for a current density ranges from 0.5 mA/cm² to 5 mA/cm² and leakage current density (J_L) was defined as the current density at $0.8V_{bk}$. 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.Mukae.⁽¹⁸⁾ The surface state density (N_s) was calculated from ϕ_b and N_d , using the relationship

$$N_s = (2N_d \epsilon \epsilon_0 \phi_b / q)^{1/2} \quad (2)$$

where ϵ is the dielectric constant of ZnO, ϵ_0 is the permittivity of vacuum, q is the electron charge.

3. Results

The phase constituents of the microwave (millimeter-wave) sintered ZnO materials are shown as X-ray diffraction patterns in Fig.1, indicating that they contain hexagonal ZnO as the main constituents, with Bi-rich ($Bi_{48}ZnO_{73}$) and spinel as secondary phase. Similar kind of phase structure was also observed for the ZnO materials densified by the conventional furnace sintering process¹². The ZnO materials can not be fully densified by fast firing process using a conventional sintering (cS) technique. The samples can only reach 88.3 % TD (theoretical density), when sintered at 1100°C-0 min with 30 °C/min heating rate (open diamonds, Fig.2a). It usually needs higher sintering temperature, longer soaking time (1200°C, 60 min) and slower temperature ramping rate (5°C/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 sintered (mS) ZnO materials is around 95.8% TD (open circles, Fig.2a), whereas that for microwave sintered (μ S) samples is only around 93% TD (open squares, Fig.2a), when the heating rate was controlled at 30°C/min. The sintered density is smaller for the samples heated in faster rate.

The mS- and μ S- processes 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°C-0 min, the grains hardly grow when conventionally sintered and has grown to around 3 μ m when microwave sintered, which is still smaller than the grain size obtained for the millimeter-wave sintered samples (~6.8 μ m). The grain size decreases for the samples sintered using a faster ramping rate, which are plotted in Fig.2b. These results reveal that using 24 GHz millimeter-wave as heating source not only enhances the densification kinetics for the ZnO materials but also increases their grain growth rate.

The electrical properties of the Bi₂O₃-based ZnO materials were characterized by their electric field-current density (E-J) and capacitance-voltage (C-V) properties, which are shown as Figs.4 and 5, respective y.

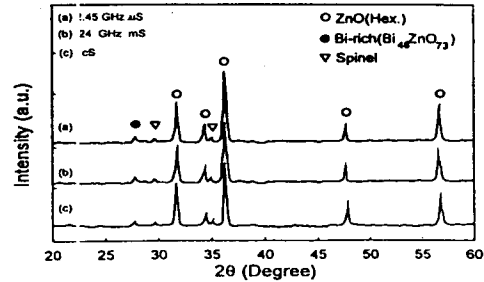


FIGURE1 X-ray diffraction patterns (CuK α) of ZnO materials densified by (a) 2.45 GHz microwave sintering (μ S) process at 1100°C (30°C/min), (b) 24 GHz millimeter-wave sintering (mS) process at 1100°C (30°C/min) and (c) conventionally furnace sintering (cS) process at 1100°C (30°C/min).

The samples conventionally sintered at 1100°C(0 min) are too leaky 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 to induce the grain growth, so as to attain large non-linearity in electrical properties (solid curve, Fig.4a).

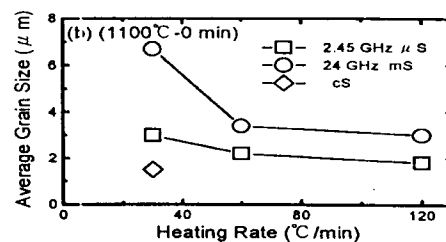
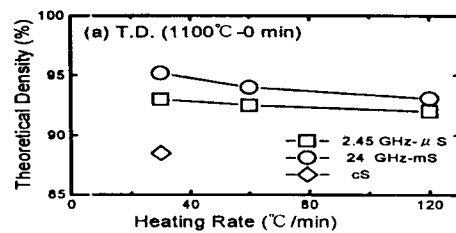


FIGURE2 The variation of (a) relative density and (b) average grain size of Bi₂O₃-based ZnO materials, densified by microwave (2.45 GHz) or millimeter-wave (24 GHz) sintering process, with 30°C/min, 60°C/min or 120°C/min heating rate.



FIGURE3 SEM micrographs of Bi₂O₃-based ZnO materials densified at 1100°C by (a) conventional furnace sintering (30°C/min), (b) 2.45 GHz microwave sintering (30°C/min) and (c) 24 GHz millimeter-wave sintering, which 30°C/min heating rate.

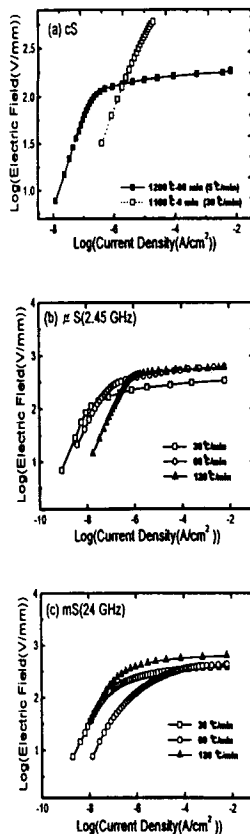


FIGURE4 The electrical field – leakage current (E-J) properties of ZnO samples (a) conventionally sintered at 1100°C-0 min (30°C/min) or 1200°C-60 min (5°C/min), (b) 2.45 GHz microwave sintered and (c) 24 GHz millimeter-wave sintered at 1100°C-0 min with 30°C/min, 60°C/min or 120°C/min heating rate.

TABLE I The varistor characteristics of Bi₂O₃-based ZnO materials densified by fast firing process, using millimeter-wave, microwave and conventional sintering techniques

Sintering Process	V _{bk} (V/mm)	J _L (10 ⁻⁶ A/cm ²)	α	N _d (10 ²⁴ m ⁻³)
mS-1100(fast) ^{a)}	600	5.55	38	1.85
µS-1100(fast) ^{b)}	580	2.1	33	0.83
cS-1200(slow) ^{c)}	172	2.52	39	2.18

Sintering Process	φ _b (eV)	N _s (10 ¹¹ cm ⁻²)	Density (%)	G.S. (µm)
mS-1100(fast) ^{a)}	2.84	7.02	93	3
µS-1100(fast) ^{b)}	2.11	4.05	92	1.8
cS-1200(slow) ^{c)}	2.55	7.23	96.4	9

^{a)} mS: millimeter-wave sintering at 1100°C-0 min with 120°C/min heating rate; the overall processing time is 17.8 minutes.

^{b)} µS: microwave sintering at 1100°C-0 min with 120°C/min heating rate; the overall processing time is 17.8 minutes.

^{c)} cS: convention furnace sintering at 1200°C-60 min with 5°C/min heating/cooling rate; the overall processing time is 528 minutes.

Table I summaries the best varistor characteristics obtained for the fastly sintered Bi₂O₃-based ZnO materials and the corresponding intrinsic parameters. It indicates, again, that the millimeter-wave and microwave sintering process needs markedly shorter soaking time than the conventional sintering process to optimize the electrical properties of the materials. The overall processing time, including temperature ramping up, soaking and temperature ramping down periods, is 17.8 min for mS- and µS- processes and is 528 min for cS-process. Moreover, the mS-process is superior to the µS-process, since the breakdown voltage (V_{bk}) of mS-samples is maintained at the same level as the V_{bk} of µS-samples (V_{bk}=580-600 V/mm), even though the grain size of mS-samples is almost twice as much as that of µS-samples. This phenomenon implies that the microstructural development for the mS-materials is more complete, such that the mS-samples own larger potential barrier height (φ_b) along their grain boundaries, which, in turn, is due to larger donor and surface state concentrations incorporated in the materials.

4. Conclusions

In this work, we observed that the Bi₂O₃-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 (α), pronounced increase in leakage current density (J_L) and marked reduction in breakdown voltage (V_{bk}), which were accounted for by the loss of Bi_2O_3 and ZnO species. Sintering at the same temperature by microwave sintering process for too short period leads to insufficient incorporation of donors and surface states, which also results in low α -and large J_L -values, but with high V_{bk} - values for ZnO samples.

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