行政院國家科學委員會補助專題研究計畫成果報告

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※　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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計畫主持人：郭正次教授
共同主持人：
計畫參與人員：張惠林, 林兆焄

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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研究(II)

(Mini-meter Wave Sintering of ZnO Varistor Ceramics(II))

計畫編號：NSC 89-2216-E-009-021

執行期限：88 年 8 月 1 日至 89 年 7 月 31 日

主持人：郭正次　交通大學材料工程系

Rapid firing of Bi_2O_3based ZnO varistor materials that includes zero minutes soaking at 1100℃ with 120℃/min heating and 145℃/min cooling rate was successfully made 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 α=38, $J_L = 5.55\times10^{-6} A/cm^2$ and $V_{bk} = 600V/mm$, whereas the intrinsic parameters of the materials are $\phi_b = 2.84eV$, $N_d = 1.85\times10^{24} m^{-3}$ and $N_S = 7.02\times10^{11} cm^{-2}$. In contrast, conventional sintering (cS) process needs higher sintering temperature (1200℃), longer soaking time (60 min) and slower ramping rate (30℃/min) to obtain ZnO materials with the same marvelous nonlinear properties as those prepared by mS-process. In additions, millimeter-wave sintering (24 GHz, mS) process enhances the densification kinetics and grain growth behavior more efficiently than the microwave sintering (2.45 GHz, μS) 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_S) and the potential barrier (ψ_b), which are presumed to be the mechanism leading to the degradation of ZnO materials'nonlinear properties.

KEYWORD: ZnO varistor, millimeter-wave sintering, 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 Bi_2O_3, Pr_6O_{11} 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-Bi_2O_3 materials. Moreover, the materials absorbed microwave power per unit volume is given by[11]

$$P = 2\pi f \varepsilon_0 \varepsilon'' |E|^2 / 2 \qquad (1)$$

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 dielectric constant 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-Bi_2O_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_2O_3 and a little amount of Mn_2O_3, CoO, NiO, Nb_2O_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 16mm in diameter and 2 mm in thickness. The green pellets, around 61% of theroetical density (TD) were microwave sintered at 1100℃ (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, 5kW) 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℃/min , 60℃/min or 120℃/min for a sintering temperature above 500℃ and then cooled in a rate of 145℃/min as soon as the sintering temperature reaches 1100℃, 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℃-0 min with 30℃/min heating rate.

The crystal structure and microstructure of the sintering samples were examined using Rigaku D/mas-

II 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 Mendelson[18] 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 ar 600℃ for 10 min to serve as electrodes. Breakdown voltage (V_{bk}) was measured at current density of 1 mA/cm^2, nonlinear coefficient (α) was estimated for a current density ranges from 0.5 mA/cm^2 to 5 mA/cm^2 and leakage current density (J_L) was deined as the current density at 0.8 V_{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.Mulae(18). The surface state density (Ns) was calculated from ϕ_b and Nd, using the relationship

$$Ns = (2Nd\varepsilon\varepsilon_o\phi_b/q)^{1/2} \quad (2)$$

Where ε is the dielectric constant of ZnO, ε_o is the permitivity 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 ($Bi_{48}ZnO_{73}$) and spinel as secondary phase. Similar kind of phase structure was also observed for the ZnO materials densified by the conventional furnace sintering process[12]. 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 ℃-0 min with30℃/min heating rate (open diamonds, Fig. 2a). It usually needs higher sintering temperature, longer soaking time (1200 ℃, 60 min) and slower temperature ramping rate (5℃/min) to achieve a sintered density as high as 96% TD. By contrast, the materials can be effectively densified, by using either microwave (2.45GHz) 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 ^{o}C/min. The sintered density is smaller for the samples heated in faster rate.

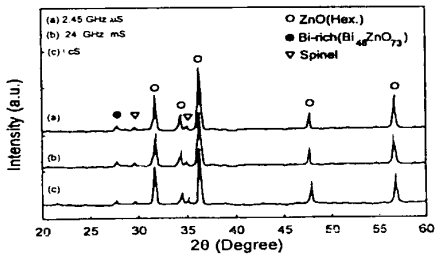

Figure 1 X-ray diffraction patterns (Cu Kα) of ZnO materials densified by (a) 2.45GHz microwave sintering (μS) process at 1100 ℃(30℃/min), (b) 24GHz millimeter-wave sintering (mS) process at 1100 ℃(30℃/min) and (c) conventionally furnace sintering (cs) at 1100 ℃(30℃/min).

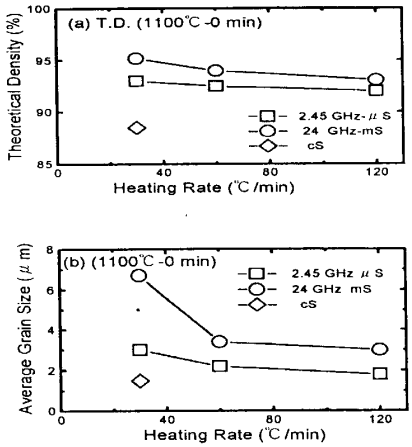

Figure 2 The variation of (a) relative density and (b) average grain size of Bi_2O_3 –based ZnO materials, densified by microwave (2.45 GHz) or millimeter-wave (2.45 GHz) sintering process, with 30℃/min, 60 ℃/min or 120℃/min heating rate.

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℃-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 Bi_2O_3-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℃(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℃-60 min (with 5℃/min ramping rate) to density 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 ℃-60min (with 5℃/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 Bi_2O_3 based ZnO materials densified at 1100 ℃ by (a) conventional furnace sintering (30 ℃/min) and (b) 2.45 GHz microwave sintering (30 ℃/min) and (c) 24GHz millimeter-wave sintering, which 30℃/min heating rate.

All the samples densitifed 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 (J_L) and breakdown voltage (V_{bk}), 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 (J_L) is smaller and the breakdown voltage (V_{bk}) is larger for samples sintered by a faster heating rate, which is associated with the smaller grain size of the materials. (α), leakage current density (J_L) and breakdown voltage (V_{bk}), 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 (J_L) is smaller and the breakdown voltage (V_{bk}) is larger for samples sintered by a faster heating rate, which is associated with the smaller grain size of the materials.

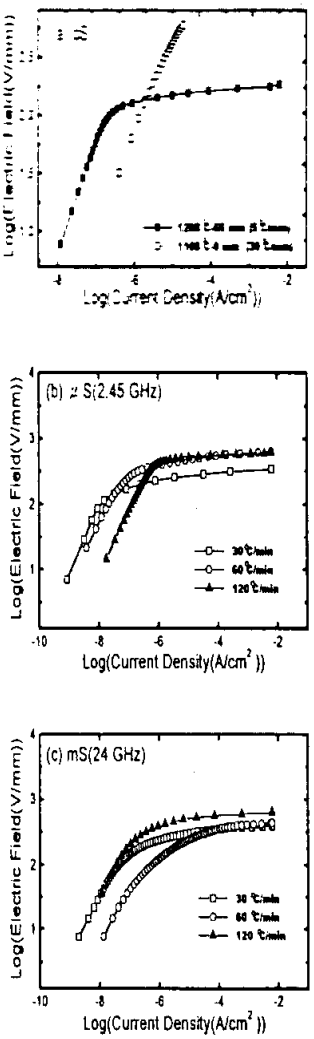

Figure 4 The electrical field-leakage current(E-J) properties of ZnO samples (a) conventionally sintered at 1100 ℃-0 min (30℃/min) or 1200-60 min (5℃/min), (b) 2.45 GHz microwave sintered and (c) 24 GHz millimeter-wave sintered at 1100 ℃-0 min with 30℃/min, 60 ℃/min or 120℃/min heating rate.

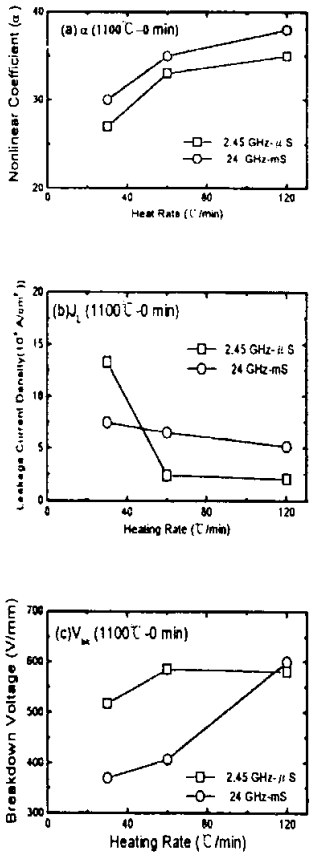

Figure 5. The variation of (a) nonlinerar coefficient, α, (b) leakage current density, J_L , and (c) breakage voltage, V_{bk} , of ZnO samples sintered at 1100 ℃-0 min with 30℃/min heating rate, by using microwave (2.45GHz) or millimeter-wave(24 GHz) sintering process.

4. Conclusion

In this work, we observed that the BiO_3- based ZnO materials can easily 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℃ 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 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 α- and leakage J_L- values, but with high V_{bk}- values for ZnO samples.

5. References

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