

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(III)

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計畫主持人：郭正次

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計畫參與人員：張惠林，林兆焄，蔡明和，林靜華

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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(III)

計畫編號：NSC 89-2216-E-009-043

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主持人：郭正次 交通大學材料科學與工程研究所

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一、中文摘要

使用毫米微波燒結方式快速燒結三氧化二鉍為基底的氧化鋅變阻陶瓷以 120 /min 升問速率至 1100 及 145 /min 冷確速度已成功達到。整個的燒結時間小於 18 分鐘且其變電阻與值為 $\rho = 38$ 與 $J_L = 5.55 \times 10^{-6} A/cm^2$ 及 $V_{bk} = 600V/mm$ 且 $\phi_b = 2.84eV$ 及 $N_d = 1.85 \times 10^{24} m^{-3}$ 與 $N_s = 7.02 \times 10^{11} cm^{-2}$ 。反之，使用傳統燒結要得到與上述方法一樣性質的 ZnO 所需的溫度要 1200 且較長的時間 (60 分鐘)，較慢的升降 (30 /min)。此外，毫米微波燒結(24 GHz, mS)製程比微波燒結(2.45 GHz, μ S) 在緻密化與晶粒成長有更快的效率，得到更好的變電阻氧化鋅材料。然而假如使用毫米微波燒結過長將過度加熱試片而產生緻密反轉效應，此的現象將減小表面狀態 (N_s) 與潛能 (ϕ_b)，其為被假設為退化氧化鋅非線性特性的因素。

關鍵詞：氧化鋅，毫米微波

Abstract

Rapid firing of Bi₂O₃based 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 $\rho = 38$, $J_L = 5.55 \times 10^{-6} A/cm^2$ and $V_{bk} = 600V/mm$, whereas the intrinsic parameters of the materials are $\phi_b = 2.84eV$, $N_d = 1.85 \times 10^{24} m^{-3}$ and $N_s = 7.02 \times 10^{11} cm^{-2}$.

$N_s = 7.02 \times 10^{11} cm^{-2}$. 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, 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_s) and the potential barrier (ϕ_b), which are presumed to be the mechanism leading to the degradation of ZnO materials' nonlinear properties.

Keywords: ZnO varistor, millimeter-wave sintering

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 Mn₂O₃, 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 16mm in diameter and 2 mm in thickness. The green pellets, around 61% of theoretical 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-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 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 0.8 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 (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 and Discussions

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 process¹². 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 with 30 /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 (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.

3.2 SEM morphology

The mS- and μ S-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 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 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 (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).

All the samples densitized 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 μ S-) 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 μ S-) 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.

4. Conclusion

In this work, we observed that the BiO₃-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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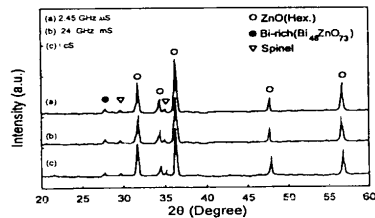


Figure 1 X-ray diffraction patterns (Cu K α) of ZnO materials densified by (a) 2.45GHz microwave sintering (μ S) process at 1100 (30 /min), (b) 24GHz millimeter-wave sintering (mS) process at 1100 (30 /min) and (c) conventionally furnace sintering (cs) at 1100 (30 /min).

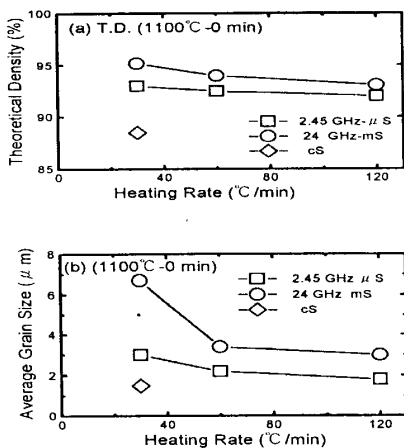


Figure 2 The variation of (a) relative density and (b) average grain size of Bi₂O₃-based ZnO materials, densified by microwave (2.45 GHz) or millimeter-wave (2.45 GHz) sintering process, with 30 /min, 60 /min or 120 /min heating rate.



Figure 3 SEM micrographs of Bi₂O₃ 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.

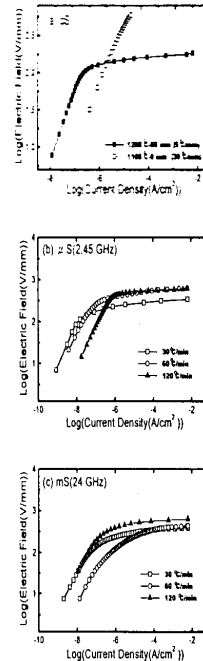


Figure 4 The electrical field-leakage current(E-J) properties of ZnO samples (a) conventionally sintered at 1100 -0 min (30 /min) or 1200-60 min (5 /min), (b) 2.45 GHz microwave sintered and (c) 24 GHz millimeter-wave sintered at 1100 -0 min with 30 /min, 60 /min or 120 /min heating rate.

