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Nonlinear electrical properties of ZnO varistors fast-fired by using millimeter-wave sintering process

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Fast firing of Bi_2O_3-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 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/cm^2 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 $N_s = 7.02 \times 10^{11}$ 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, 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 height (ϕ_b), which are presumed to be the mechanism leading to the degradation of ZnO materials' nonlinear properties.

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]

$$P = \frac{2\pi f \varepsilon_0 \varepsilon'' |E|^2}{2}, \quad (1)$$

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 study, 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. The ZnO samples are composed of 3 mol% Bi_2O_3 and a small amount of Mn_3O_4, CoO, NiO, Nb_2O_5 and Na-glass as microstructure stabilizers and nonlinearity promoting elements. The samples, which were uniaxially pressed at 750 kgf/cm^2 into disks of 16 mm diameter and 2 mm thickness and around 61% of theoretical density (T.D.), were microwave (or millimeter-wave) 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 from alumina-silica fiberboard, which contains six SiC rods placed at inner wall as susceptors. The temperature profile was measured using Pt-13% Rh thermocouple placed in contact with 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 cS process, with the sample temperature profile as the μS (or mS) process.

The crystal structure and microstructure of the sintering samples were examined using a Rigaku D/max-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 Mendelson [18] with a multiple factor of 1.56. The V-I properties of these samples were recorded using a Keithley 237 I-V electrometer in dc source after the silver paste was applied to the sample surface and fired at 600°C for 10 min to serve as electrodes. The breakdown voltage (V_{bk}) was measured at current density of 1 mA/cm^2, the nonlinear coefficient (α) was estimated for the current density ranges from 0.5 mA/cm^2 to 5 mA/cm^2 and the leakage current density (J_L) was defined as the current density at 0.8 V_{bk}. The C-V measurements were carried out at room temperature using a HP4272A capacitance meter. The electrical characteristics, including the barrier height (ϕ_b) and donor density (N_d), were determined from C-V data, using the model proposed by Mukae *et al.* [18]. The surface state density (N_s) was calculated from ϕ_b and N_d, using the relationship

$$N_s = \left(\frac{2N_d\varepsilon\varepsilon_0\phi_b}{q}\right)^{1/2}, \qquad (2)$$

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

3. Results

3.1. Fast firing process

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 process [12]. 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

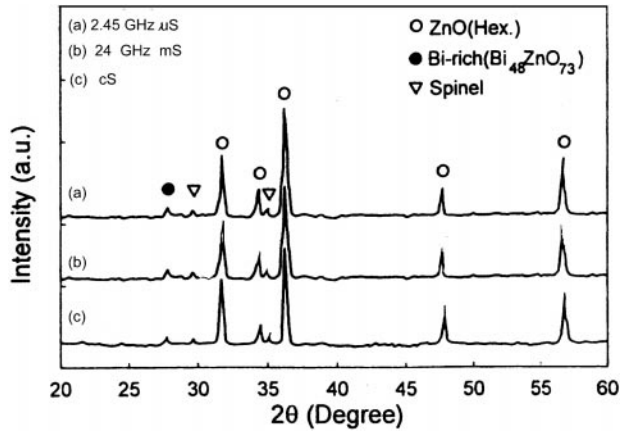

Figure 1 X-ray diffraction patterns (Cu K_α) of ZnO materials densified by (a) 2.45 GHz microwave sintering (μS) process at 1100°C (30°C/min), (b) 24 GHz millimeter-wave sintering (mS) process at 1100°C (30°C/min) and (c) conventionally furnace sintering (cS) process at 1100°C (30°C/min).

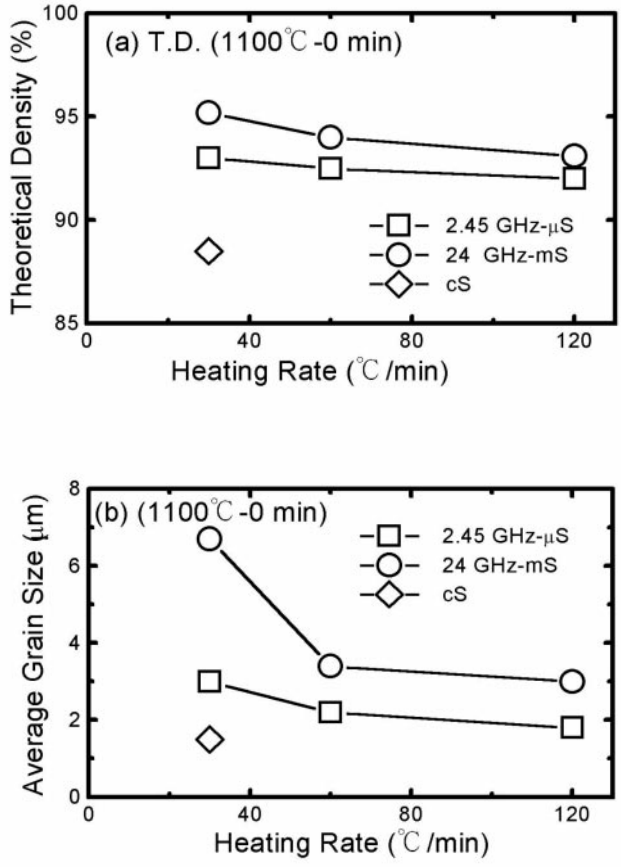

Figure 2 The variation of (a) theoretical density and (b) average grain size of Bi_2O_3-based ZnO materials, densified by microwave (2.45 GHz) or millimeter-wave (24 GHz) sintering process, with 30°C/min, 60°C/min or 120°C/min heating rate.

slower temperature ramping rate (5°C/min) to achieve a sintered density as high as 96% T.D. By contrast, the materials can be effectively densified, 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% T.D. (open circles, Fig. 2a), whereas that for microwave sintered (μS) samples is

only around 93% T.D. (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 μS-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 μm when microwave sintered, which is still smaller than the grain size obtained for the millimeter-wave sintered samples ($\sim$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 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 Bi_2O_3-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, respectively. The samples conventionally sintered at 1100°C(0 min) are too leaky to exhibit good enough nonlinear properties

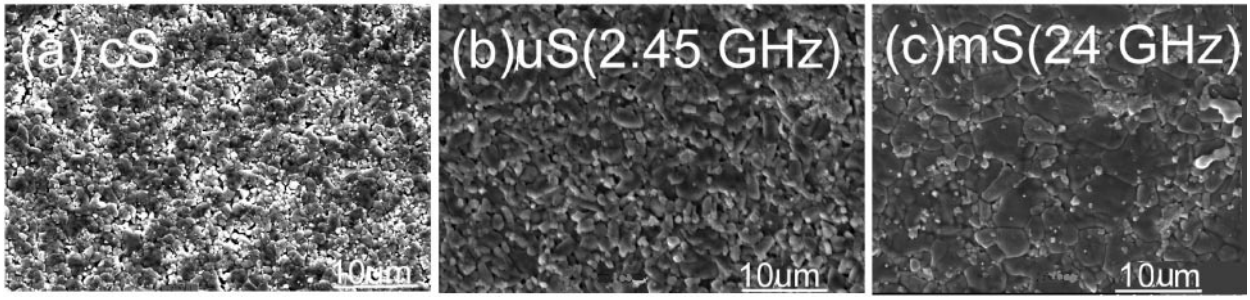

Figure 3 SEM micrographs of Bi_2O_3-based ZnO materials densified at 1100°C by (a) conventional furnace sintering (30°C/min), (b) 2.45 GHz microwave sintering (30°C/min) and (c) 24 GHz millimeter-wave sintering, which 30°C/min heating rate.

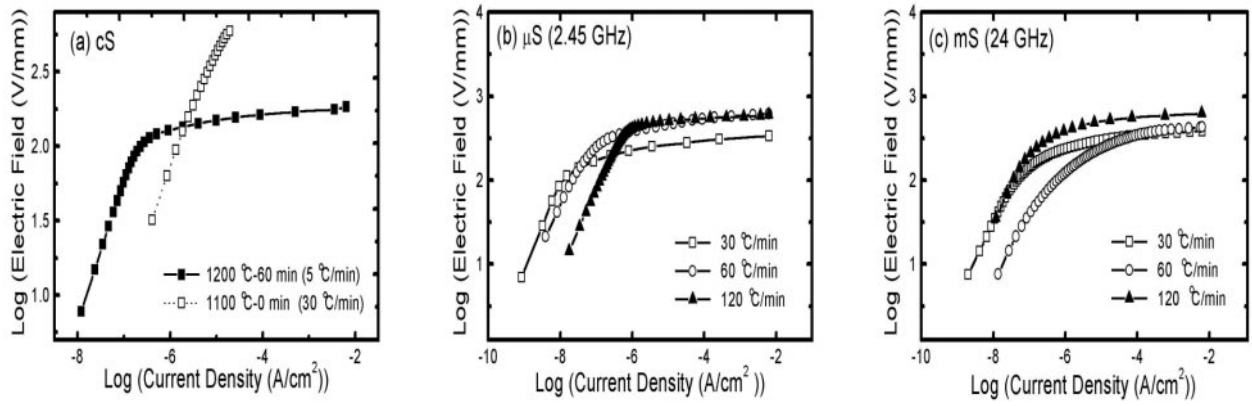

Figure 4 The electrical field–leakage current (E-J) properties of ZnO samples (a) conventionally sintered at 1100°C-0 min (30°C/min) or 1200°C-60 min (5°C/min), (b) 2.45 GHz microwave sintered and (c) 24 GHz millimeter-wave sintered at 1100°C- 0 min with 30°C/min, 60°C/min or 120°C/min heating rate.

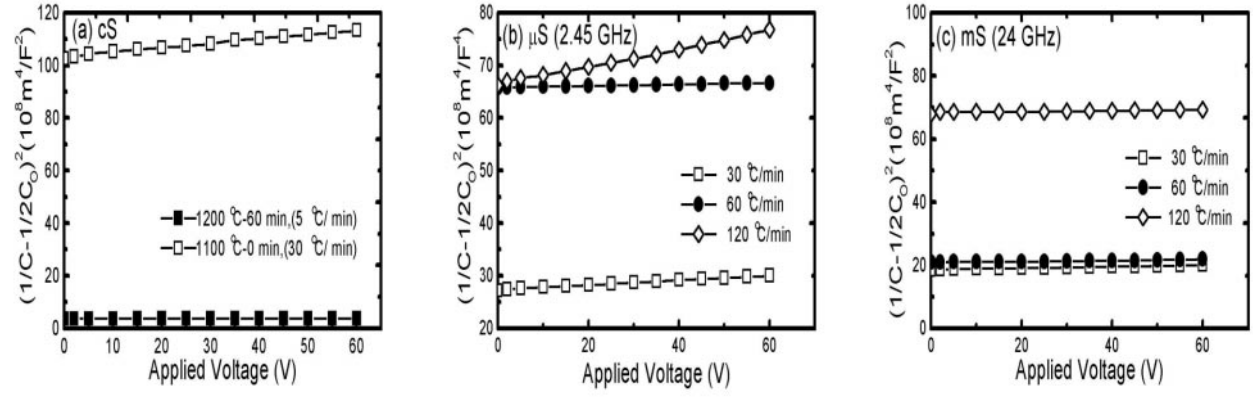

Figure 5 The capacitance–voltage (C-V) properties of ZnO samples (a) conventionally sintered at 1100°C-0 min (30°C/min) or 1200°C-60 min (5°C/min), (b) 2.45 GHz microwave sintered and (c) 24 GHz millimeter-wave sintered at 1100°C- 0 min with 30°C/min, 60°C/min or 120°C/min heating rate.

(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 nonlinearity in electrical properties (solid curve, Fig. 4a).

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. 6a–c for nonlinear coefficient (α), leakage current density (J_L) and breakdown voltage (V_{bk}), respectively. The nonlinear coefficients (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 sintering 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. The intrinsic parameters derived from C-V curves of the ZnO samples are shown in Fig. 7a–c, indicating that the potential barrier height (ϕ_b) increases, with the donor density (N_d) and surface state density (N_s) decreases as the heating rate increases.

Table I summaries the best varistor characteristics obtained for the fast sintered Bi_2O_3-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

TABLE I Varistor characteristics of Bi_2O_3-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	ϕ_b (eV)	N_d (10^{24} m^{-3})	N_s (10^{11} cm^{-2})	G.S. (μm)	Density (%)
mS-1100(fast)[a)]	600	5.55	38	2.84	1.85	7.02	3	93
μS-1100(fast)[b)]	580	2.1	33	2.11	0.83	4.05	1.8	92
cS-1200(slow)[c)]	172	2.52	39	2.55	2.18	7.23	9	96.4

[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.

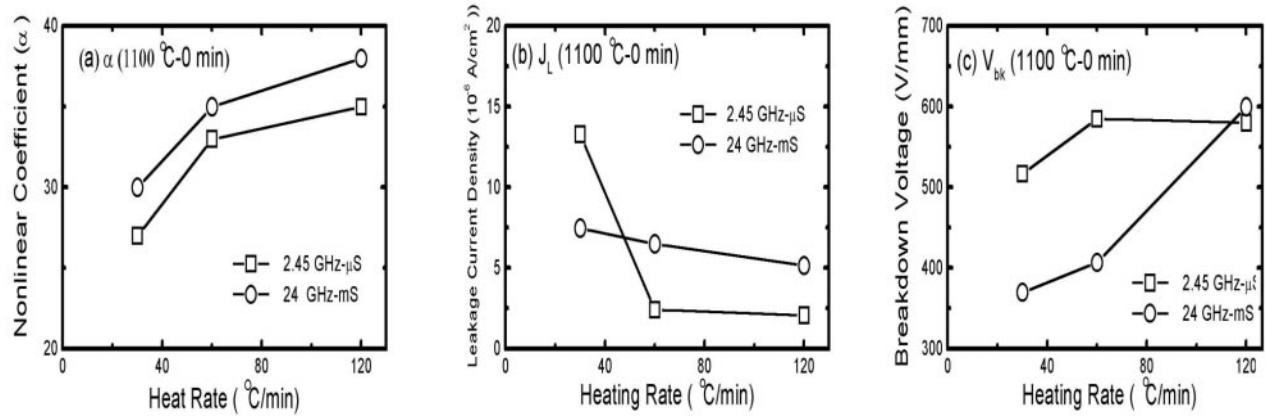

Figure 6 The variation of (a) nonlinear coefficient, α, (b) leakage current density, J_L, and (c) breakdown voltage, V_{bk}, of ZnO samples sintered at 1100°C-0 min, with 30°C/min heating rate, by using microwave (2.45 GHz) or millimeter-wave (24 GHz) sintering process.

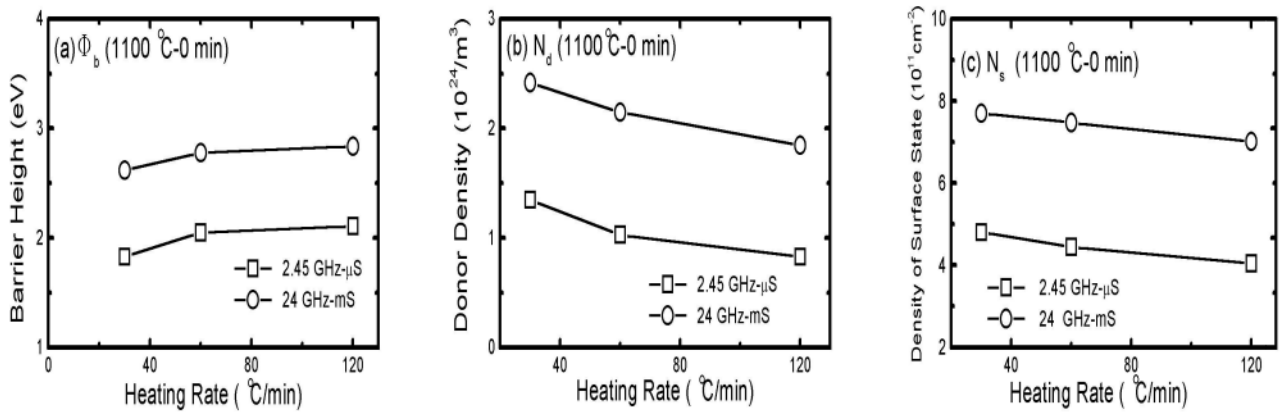

Figure 7 The variation of (a) potential barrier height, ϕ_b, (b) donor density, N_d, and (c) surface state density, N_s, of ZnO samples, microwave (2.45 GHz) or millimeter-wave (24 GHz) sintered at 1100°C with 30°C/min heating rate.

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 microstructure 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.

3.2. Soaking time effect

To understand how the millimeter-wave sintering process improves the densification kinetics, microstructure development and the associated varistor characteristics of ZnO materials, the samples were sintered at 1100°C and soaked for 0–10 min, with 30°C/min heating rate and 145°C/min cooling rate. The effect of soaking time on the densification behavior of the Bi_2O_3-based ZnO materials is shown in Fig. 8a, revealing that a density higher than 95%TD can be achieved for the samples densified by millimeter-wave sintering (mS) process, even when sintered with zero soaking time. The ultimate density can be achieved for the samples densified by the this process is 96.0% T.D., which corresponds to 1100°C-5 min mS-sintered samples. A density reversion phenomenon occurs for samples sintered for longer soaking time (10 min), shown as closed circle in Fig. 8a. Such a phenomenon will impose significant effect on electrical properties of the samples, which will be discussed shortly. The density of microwave sintered samples, which is only 93% T.D. when soaked for 0 min, increases monotonously with soaking time without the occurrence of density reversion phenomenon and reaches a much higher density (∼96.5% T.D.) for those soaked for 10 min. The sintered density for the samples prepared by conventional sintering (cS) process is always small when soaking time is short (0–10 min). It takes 60 min to achieve a density as high as 96% T.D., when conventionally sintered (closed diamonds, Fig. 8a).

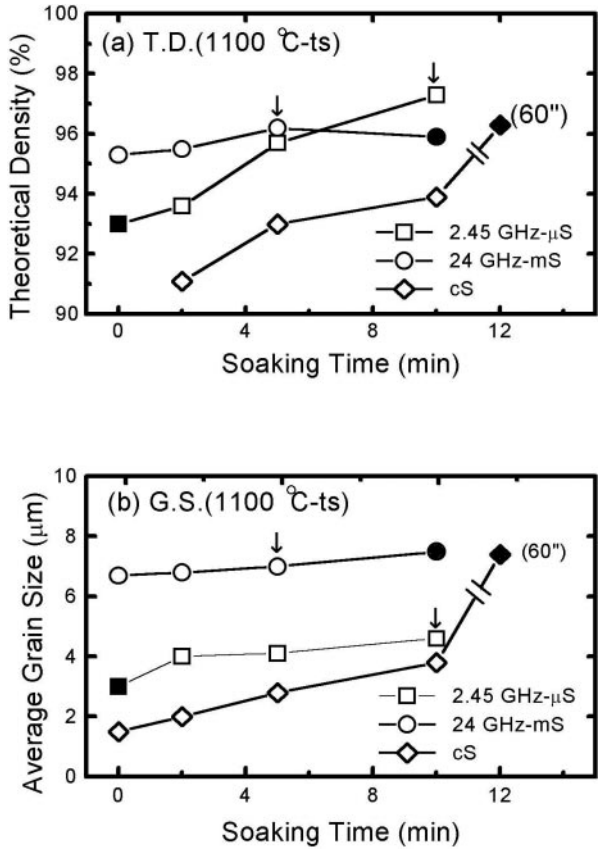

Figure 8 The variation of (a) theoretical density and (b) average grain size with soaking time for ZnO samples, microwave (2.45 GHz) or millimeter-wave (24 GHz) sintered at 1100°C, and those of the materials conventional sintered at 1100°C for 0–60 min.

Microwave (or millimeter-wave) sintering process not only enhances the densification of ZnO materials, but also improve their grain growth behavior. When sintered at 1100°C for 0 min, the grains hardly grow for cS-processed samples (<1.5 μm), but have already grown to a size as large as 3 μm for μS-processed samples and to about 6.5 μm for mS-processed samples, which are illustrated in Fig. 8b. The grains of mS-samples need only 0 min soaking time at 1100°C to reach the matured size (∼6.5 μm), whereas those of μS-samples take at least 5 min at the same temperature to do so. The grain size of mS- (or μS-) materials increases only slightly with soaking time after the grains reached the matured size. By contrast, it needs at least 60 min for cS-process to result in materials with the same granular size as those sintered by mS-process (solid diamonds, Fig. 8b). These results imply that the activation energy for grain growth is also markedly reduced at the presence of millimeter-wave (or microwave) and the millimeter-wave is more efficient than the microwave in enhancing the grain growth of the materials.

The electric field-current density (E-J) properties of thus obtained ZnO materials are shown in Fig. 9, whereas the corresponding varistor parameters, including nonlinear coefficient (α), leakage current density (J_L) and breakdown voltage (V_{bk}) were derived from the E-J curves and are shown in Fig. 10a–c, respectively. The varistor characteristics of the 1100°C sintered cS-samples are substantially inferior to those of mS- (or μS-) samples, viz. the nonlinearity (α) is smaller, the leakage current density (J_L) is larger and breakdown voltage (V_{bk}) is higher. Such a phenomenon is apparently due to insufficient densification and incomplete microstructure development of the cS-samples. Such an assumption is supported by the phenomenon, that once the sintered density of cS-materials was raised to 96% T.D. and the grain size of these samples was increased to around 7 μm, by extending the soaking time in cS-process to 60 min, the varistor characteristics of the samples can be increased to a level comparable with the varistor characteristics of mS- (μS-) samples, viz. $\alpha = 28$, $J_L = 3 \times 10^{-6}$ A/cm^2 and $V_{bk} = 270$ V/mm (solid diamonds in Fig. 10).

The nonlinearity (α) of μS-samples increases with soaking time monotonously, which is of the same trend as the soaking time dependence of the density of the samples (arrows, Figs 10a and 8a). By contrast, the nonlinearity (α) of mS-samples reaches a maximum value, in accompanied with lowest leakage current density, for those which soaked for 5 min and degrades

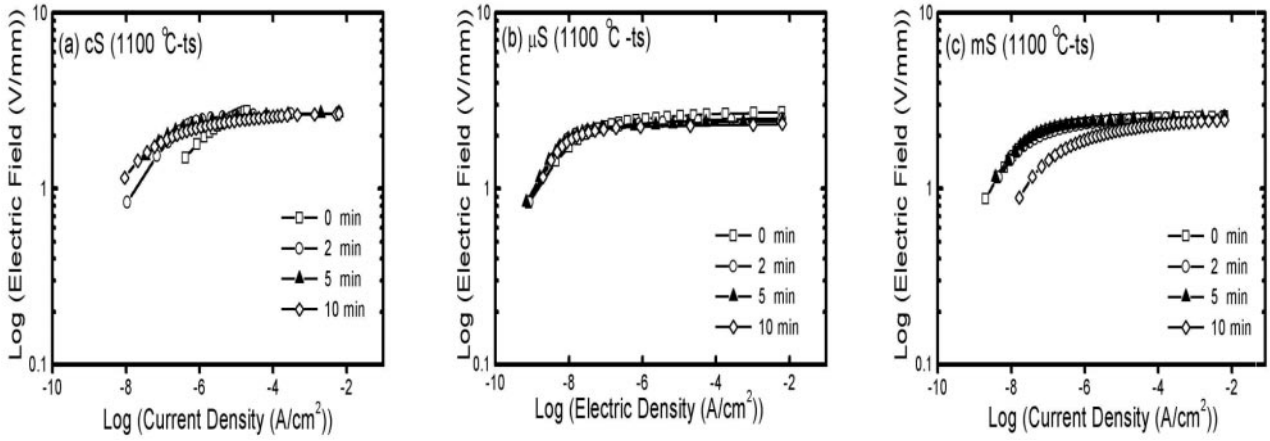

Figure 9 The electrical field–leakage current (E-J) properties of ZnO samples, (a) conventionally, (b) 2.45 GHz microwave, and (c) 24 GHz millimeter-wave sintered at 1100°C with 0–10 min soaking time.

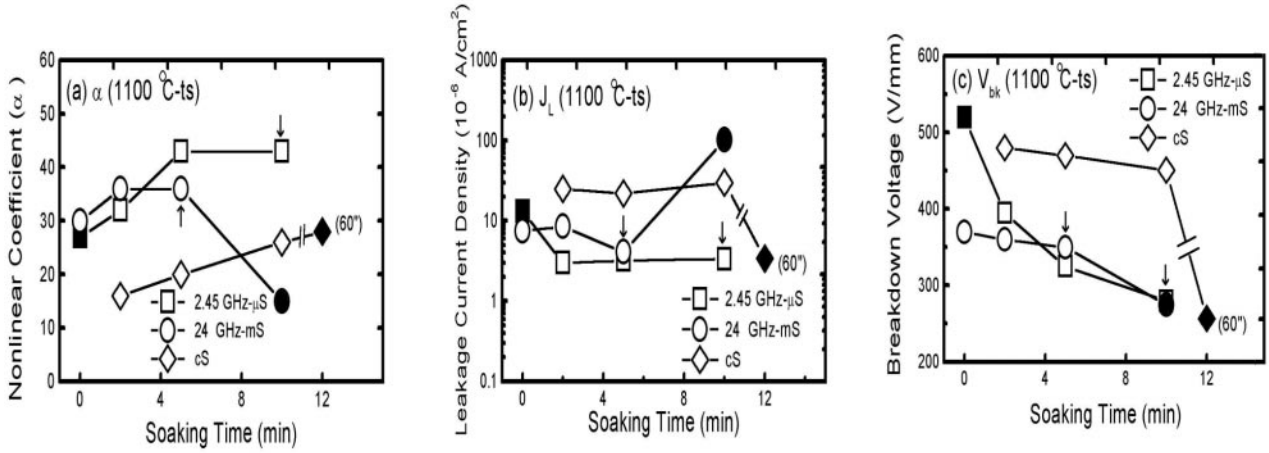

Figure 10 The variation of (a) nonlinear coefficient, α, (b) leakage current density, J_L, and (c) breakdown voltage, V_{bk}, of ZnO samples microwave (2.45 GHz) or millimeter-wave (24 GHz) sintered at 1100°C, with soaking time.

pronouncedly for the samples soaked for longer period (i.e., 10 min). The degradation of varistor properties is intimately correlated with the density reversion phenomenon shown in Fig. 8a. Restated, the nonlinearity (α) decreases dramatically and the leakage current density (J_L) increases abruptly when the samples are overfired, which will be further discussed shortly.

The optimized varistor characteristics obtainable for Bi_2O_3-based ZnO materials sintered by either millimeter-wave, microwave or conventionally process are indicated by arrows in Fig. 10. It reveals, again, that the millimeter-wave sintering process is superior to the microwave sintering process, since the former needs shorter soaking time to optimize the electrical properties of the materials. For the materials sintered for too long soaking time, such as mS (1100°C- 10 min), the nonlinear properties (α) degrades in accompanied with the occurrence of density reversion phenomenon. The leakage current density (J_L) is large and the breakdown voltage (V_{bk}) is small (solid circles, Fig. 10). By contrast, for the materials sintered for too short soaking time, such as cS (1100°C-10 min) and μS (1100°C-0 min) samples, the nonlinear properties (α) are also small, but in accompanied with large leakage current density (J_L) and high the breakdown voltage (V_{bk}) (solid squares, Fig. 10). These phenomena are ascribed to the insufficient development of the granular structure, since the samples possess small grain microstructure.

4. Discussion

The intrinsic parameters, including the potential barrier height (ϕ_b), donor density (N_d) and surface state density (N_s), were derived from the capacitance-voltage (C-V) properties of these Bi_2O_3-based ZnO materials (not shown). The analyses indicate that the potential barrier height (ϕ_b) of cS-samples sintered for 2–10 min (open diamonds, Fig. 11a) is markedly larger than those of mS- (or μS-) samples, although the cS-samples possess very small nonlinear coefficient (α). Fig. 11b and c indicates that these cS-samples are actually insufficiently sintered, since both the donor density (N_d) and the surface state density (N_s) are small. Such an assumption is supported by the phenomenon that the cS (1100°C-60 min) samples also exhibit good nonlinear electric properties ($\alpha = 28$, $J_L \leq 3.4 \times 10^{-6}$ A/cm^2 and $V_{bk} = 257$ V/mm), when they own high density (96.3% T.D.), large grain size (7.4 μm), and contain large proportion of donor and surface density ($N_d = 2.2 \times 10^{24}$ cm^{-3} and $N_s = 7.47 \times 10^{11}$ cm^{-2}). Similarity, the phenomenon that μS

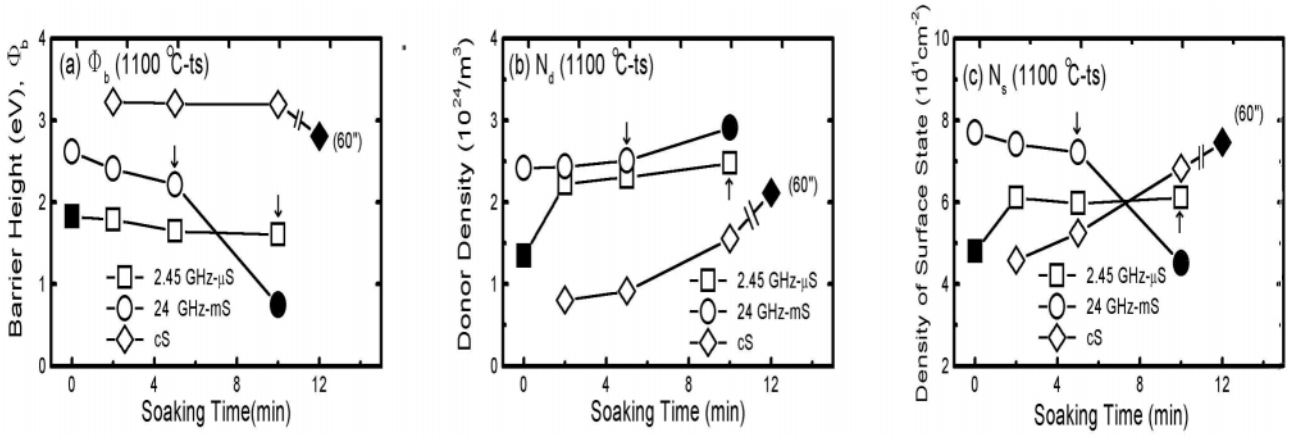

Figure 11 The variation of (a) potential barrier height, ϕ_b, (b) donor density, N_d and (c) density of surface state, N_s, of ZnO samples microwave (2.45 GHz) or millimeter-wave (24 GHz) sintered at 1100°C, with soaking time.

(1100°C-0 min) samples (solid squares, Fig. 11a) show low nonlinear properties ($\alpha = 27$), in accompanied with large potential barrier high ($\phi_b = 1.83$ eV), can also be ascribed to the insufficient development of the materials' microstructure, since these samples also contain small proportion of donor (N_d) and surface state (N_s) density (Fig. 11b and c).

By contrast, small nonlinear coefficient for mS (1100°C-10 min) samples (solid circles, Fig. 11a) is attributed to the overfiring of the materials, since Fig. 11b and c indicate that the samples still contain large proportion of donors (N_d), but possess insufficient amount of surface states (N_s). Therefore, the samples do not have high enough potential barrier (ϕ_b) and exhibit low nonlinearity (α), high leakage rate (J_L), small breakdown voltage (V_{bk}). The decrease in surface state concentration (N_s) is presumably due to the loss of volatile species, such as ZnO and Bi_2O_3, along grain boundaries, which can also account for the density reversion phenomenon described in Fig. 8a. Restated, both the underfired and overfired ZnO materials show degraded varistor characteristics and only the properly sintered samples exhibit good nonohmic electrical properties. All the varistor characteristics (α, J_L and V_{bk}) and intrinsic electric parameters (ϕ_b, N_d and N_s) vary insignificantly with the soaking time when the ZnO materials are properly sintered.

5. Conclusions

In this study, we observed that the Bi_2O_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 (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 in corporation 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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