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On the microwave sintering technology for improving the properties of semiconducting electronic ceramics

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Abstract

Microwave (millimeter wave) sintering technology used for enhancing the densification behavior and electrical properties of ZnO electronics ceramic materials was described. Successfulness in application of such a novel technique to sinter ceramics relies heavily on the microwave (millimeter-wave) absorption efficiency of the materials. Semiconducting oxides such as Bi_2O_3-doped ZnO materials perform satisfactorily in microwave (millimeter-wave) sintering. Using susceptors to facilitate absorption efficiency of the samples greatly improves the sinterability of the materials. The advantage of the microwave (millimeter-wave) sintering process over the conventional sintering technique is best demonstrated by fast firing of Bi_2O_3-based ZnO varistor materials, in which, the whole sintering process required only 18 min. The varistor characteristics obtainable are: $\alpha = 38$, $J_L = 55.5 \times 10^{-6}$ A/cm^2 and $V_{bk} = 600$ V/mm.

Keywords: Electronics ceramic; Microwave sintering; ZnO

1. Introduction

It is generally accepted that the microwave sintering (μS) process can densify ceramic materials at a very rapid rate and at a substantially lower temperature than the conventional sintering (cS) process.[1,2] Higher quality materials are produced by microwave heating techniques than by using conventional heating methods.[3–5] 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.[6–8] These ZnO-based varistors are, therefore, extensively employed as transient surge suppressers to protect electronic circuits against dangerous abnormal high voltages.[9–11]

In this study, the correlation between the microwave absorption characteristics of the materials and their basic properties is discussed. The densification behavior of ZnO–Bi_2O_3 based ceramics prepared by microwave (millimeter-wave) sintering was examined to determine the advantage of these sintering processes over conventional sintering processes.

2. Experimental procedure

The samples used in the sintering experiments were prepared from a commercial high-purity oxide powder, including Al_2O_3, SiC and ZnO. The oxide powders were microwave (or millimeter-wave) heated in an applicator. The 2.45 GHz microwaves generated from a magnetron (CEM, MAS-700, 1 kW) or the 24 GHz microwaves generated from a gyrotron (Micramics Inc, 5 kW) were used. The varistor samples were prepared from a commercial high-purity (>0.999) zinc oxide powder containing 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 were microwave (or millimeter-wave) sintered at 1100°C in an applicator. The sample temperature was measured using Pt-13%Rh thermocouple placed in contact with the sample surface. The samples were heated at a rate of

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120°C/min and then cooled at a rate of 145°C/min as soon as the sintering temperature reached 1100°C, (0 min soaking time). For comparison, the samples were also densified by a conventional sintering (cS) process, with the same temperature profile as for the μS process.

The density of the sintered materials was measured by Archimedas method. The crystal structure and microstructure of the sintered samples were examined using a Rigaku D/mas-IIB X-ray diffractometer (XRD) and Hitachi S3500 scanning electron microscope (SEM), respectively. 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 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.[12]

3. Results and discussion

3.1. Sintering behavior of ceramics

The most important factor determining whether a material is sinterable or not is the microwave absorption efficiency (η). Such behavior is best demonstrated by the time evolution of temperature of the materials (Fig. 1), the temperature profile of semiconducting oxides (ZnO) under action of 24 GHz milli-meter wave. The temperature of ZnO materials increased rapidly at a rate of about 60°C/min in regime 1. The heating rate decreases markedly, to around 35°C/min, for a sample temperature higher than 950°C. The thermal runaway phenomenon is unlikely to occur, since the heating rate slows down at the high temperature regime. These materials are thus categorized as well-behaved materials. The semiconducting ZnO materials also absorb the 2.45 GHz microwave efficiently and the heating rate slows down at high temperature such that the thermal run away phenomenon is unlikely to occur. Therefore, the ZnO materials are also categorized as microwave sinterable materials at 2.45 GHz. The other important characteristic influencing the microwave sintering behavior of the materials is the efficiency of heat conduction in the materials, since it can result in non-uniformity in sample temperature. As illustrated in Fig. 1, the surface temperature markedly lags behind the core temperature for all the temperature range. The temperature difference can be as large as 380°C. The phenomenon that the surface temperature of the samples is always lower than the core temperature is expected, since the heat is generated directly in the materials via the absorption of microwaves and then transported outward by thermal conduction. Large heat loss at the surface of the samples to the surrounding insulators results in significantly lower surface temperature for the samples. Such a temperature difference can lead to pronounced microstructural inhomogeneity between the core and the surface regions of the samples. A technique that can amend such a deficiency is urgently needed. Utilization of an auxiliary heater surrounding the samples to reduce the heat loss from the surface of the samples is a probable solution. A material, which absorbs the microwaves efficiently, is stable at high temperature and can endure temperature cycling, would be a good material for serving as susceptors. The millimeter-wave absorption behavior of the insulating materials, including Al_2O_3 and SiC, have been examined for this purpose.

The Al_2O_3 materials are essentially non-absorbing to millimeter-waves at all power levels and cannot be used as susceptors, but they are, however, good crucible materials. By contrast, the SiC materials absorb the millimeter-wave so efficiently that they can be heated up effectively even for small millimeter-wave power (Fig. 2). This is a very useful characteristic, since when used as susceptors, they can indirectly heat the samples to a high enough temperature, triggering the microwave absorption of the samples. Fig. 2 reveals that the SiC materials

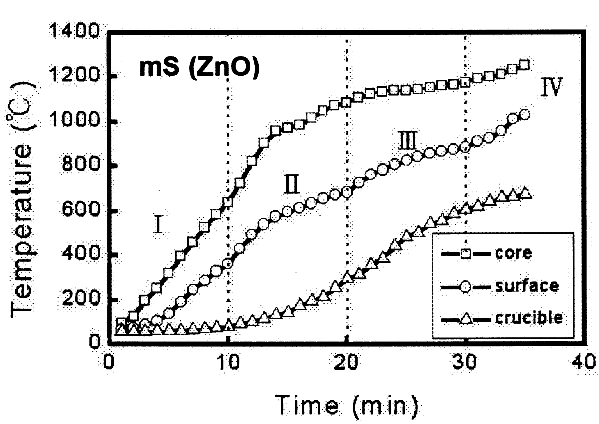

Fig. 1. The temperature–time profile of core, surface and crucible of ZnO materials heated by milli-meter wave.

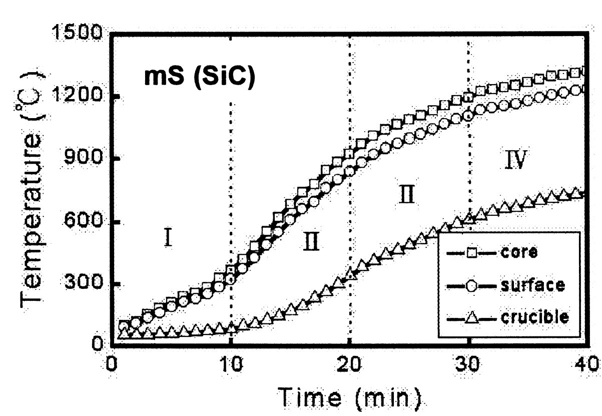

Fig. 2. The temperature–time (T–t) characteristics of SiC materials heated by millimeter-wave (24 GHz).

not only absorb the microwave power efficiently but also possess very good thermal conductivity such that the difference in core and surface temperature remains at a very small value ($\Delta T \leqslant 90°C$) even at a temperature as high as 1300°C. These materials also possess self-regulation capability, that is, the heating rate slows down and the samples temperature saturates at high microwave power levels. Another feature which makes utilization of SiC susceptors a useful technique is that above the temperature at which the samples start to absorb the millimeter-wave efficiently, the proportion of power absorbed by the SiC materials diminishes abruptly. The incident power can thus be fully utilized to heat up the samples for sintering process.

How the utilization of SiC susceptors improves the microwave sintering process is illustrated in Fig. 3, showing that the temperature profile of the surface region (closed circles), which was previously hundreds of degrees lower than the core region, is now only slightly smaller than the core temperature (open squares). Restated, the temperature uniformity of the samples during microwave sintering has been tremendously improved due to the application of SiC susceptors. Moreover, the temperature profile of the auxiliarily heated ZnO materials is exactly the same as that without the SiC susceptors (cf. Figs. 1 and 3). The utilization of SiC susceptors does not hinder the millimeter-wave absorption efficiency of the ZnO materials. The SiC materials also absorb microwave power very efficiently and possess self-regulation capability in 2.45 GHz frequency regime, that is, the heating rate slows down and the sample temperature saturates, in the high microwave power regime.

3.2. Fast firing of ZnO varistor materials

The microwave sintered ZnO materials contain phase constituents similar to those observed for the ZnO materials densified by the conventional furnace sintering process. The ZnO materials can only reach 88.3% TD (theoretical density), when sintered at 1100°C — 0 min with 30°C/min heating rate by the conventional sintering process. 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, using either microwave (2.45 GHz) or millimeter-wave (24 GHz) sintering process. The sintered density attainable for millimeter-wave sintered (mS) ZnO materials is around 93% TD, whereas that for microwave sintered (μS) samples is only around 92% TD, when sintered at 1100°C (0 min) with the heating rate controlled at 120°C/min. This evidence implies that the densification rate is markedly enhanced in these process.

The mS- and μS- processes also impose pronounced enhancement on the grain growth behavior of the ZnO materials. For the samples sintered at 1100°C — 0 min, the grains hardly grow when conventionally sintered, but have grown to around 1.8 μm when microwave sintered and to ~ 3 μm when millimeter-wave sintered. These results reveal that using 24 GHz millimeter-wave as heating source not only improves the densification kinetics for the ZnO materials but also enhances their grain growth rate.

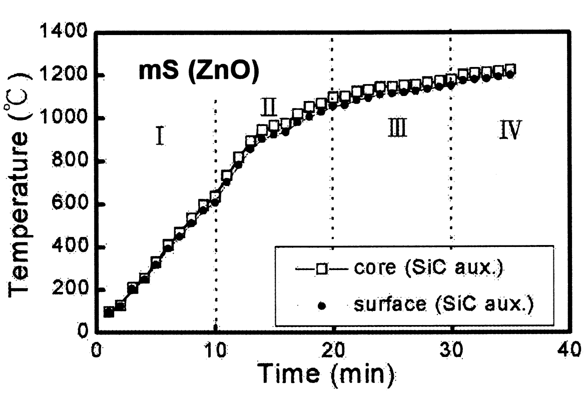

Fig. 3. The sintering profile of the ZnO materials, using application of SiC rods as susceptors.

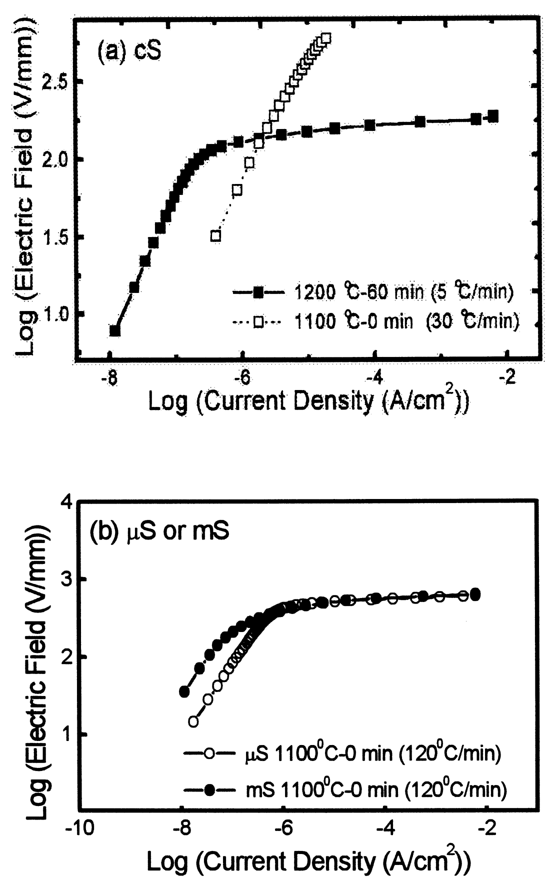

Fig. 4. The electrical field–leakage current (E–J) properties of ZnO samples (a) conventionally sintered at 1100°C — 0 min (30°C/min) or 1200°C — 60 min (5°C/min); (b) 2.45 GHz microwave sintered (μS) or 24 GHz millimeter-wave sintered (mS) at 1100°C — 0 min with 120°C/min heating rate.

Table 1
Varistor characteristics[a] of Bi_2O_3-based ZnO materials densified by fast firing process, using millimeter-wave, microwave and conventional sintering techniques

Sintering process	D (% TD)	G.S. (μm)	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})
mS[b]	93	3	600	5.55	38	2.84	1.85	7.02
μS[b]	92	1.8	580	2.1	33	2.11	0.83	4.05
cS[c]	96.4	9	172	2.52	39	2.55	2.18	7.23

[a] D: % of theoretical density; G.S.: grain size; V_{bk}: breakdown voltage; J_L: leakage current density; α: nonlinearity; ϕ_b: work function; N_d: surface state density.
[b] mS (μS): millimeter-wave (microwave) sintering at 1100°C — 0 min with 120°C/min heating rate; the overall processing time is 17.8 min.
[c] cS: convention firnace sintering at 1200°C — 60 min with 5°C/min heating/cooling rate; the overall processing time is 528 min.

The electrical properties of the Bi_2O_3-based ZnO materials were characterized by their electric field–current density (E–J), which are shown as Fig. 4. The samples conventionally sintered at 1100°C (0 min) are too leaky to exhibit good enough nonlinear properties (open squares, 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 squares, Fig. 4a).

All the samples densified by millimeter-wave or microwave sintering process exhibit good nonlinear properties, as shown in Fig. 4b. The varistor parameters, including nonlinear coefficient (α), leakage current density (J_L) and breakdown voltage (V_{bk}), were derived from the E–J curves. The intrinsic parameters were derived from C–V curves (not shown) of the ZnO samples. The α-values of the millimeter-wave sintered materials are much higher than those of the microwave sintered materials. The varistor and intrinsic parameters for the samples sintered using a 120°C/min heating rate are listed in Table 1, which 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 the cS- process. Moreover, the mS-process is superior to the μS-process, since the microstructure development for the mS-materials is more complete, such that the mS-samples have larger potential barrier height (ϕ_b) along their grain boundaries, This, in turn, is due to larger donor and surface state concentrations incorporated in the materials.

4. Conclusions

The heating profiles of functional ceramics, ZnO, and refractory ceramics, Al_2O_3 and SiC, in millimeter-wave and microwave sintering processes were examined. ZnO materials are categorized as high absorption materials to both 24 GHz millimeter-wave and 2.45 GHz microwave sources. They are all well-behaved during microwave sintering process. Using SiC materials as susceptors to absorb the microwave (millimeter-wave), heating up the surface of the samples, can greatly improve the temperature uniformity of the samples. Moreover, millimeter-wave sintering process can enhance the densification rate and hence improve the varistor characteristics of the ZnO materials to a greater extent than the microwave sintering process.

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