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Two-Step Sintering of Nanocrystalline ZnO Compacts: Effect of Temperature on Densification and Grain Growth

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Two-step sintering (TSS) was applied on nanocrystalline zinc oxide (ZnO) to control the accelerated grain growth occurring during the final stage of sintering. The grain size of a high-density (>98%) ZnO compact produced by the TSS was smaller than 1 μm, while the grain size of those formed by the conventional sintering method was ~4 μm. The results showed that the temperature of both sintering steps plays a significant role in densification and grain growth of the nanocrystalline ZnO compacts. Several TSS regimes were analyzed. Based on the results obtained, the optimum regime consisted of heating at 800°C (step 1) and 750°C (step 2), resulting in the formation of a structure containing submicrometer grains (0.68 μm). Heating at 850°C (step 1) and then at 750°C (step 2) resulted in densification and grain growth similar to the conventional sintering process. Lower temperatures, e.g., 800°C (step 1) and 700°C (step 2), resulted in exhaustion of the densification at a relative density of 86%, above which the grains continued to grow. Thermogravimetric analysis results were used to propose a mechanism for sintering of the samples with transmission electron micrographs showing the junctions that pin the boundaries of growing grains and the triple-point drags that result in the grain-boundary curvature.

I. Introduction

The recent focus on nanocrystalline materials is due to their interesting electrical,[1–3] optical,[4,5] mechanical,[6,7] or chemical[8] properties. The high surface area of the particles provides a substantial driving force for sintering, which will reduce the sintering activation energy. Lower sintering temperature will then become feasible.[9–12] Despite these excellent features, the very fine size can also lead to such problems as agglomeration, surface contamination, anisotropy, grain coarsening, and exaggerated grain growth.[12,13]

Zinc oxide (ZnO) is an attractive ceramic material usable in electrical, optical, and medical applications.[1,2,4,14,15] Owing to photoluminescence properties, ZnO is used in green displaying devices. Wang and Gao[4] recently reported that because of the high volume of grain boundaries in the as-produced nanocrystalline ZnO ceramics by spark plasma sintering (SPS), these materials produce both strong-green and weak-ultraviolet emissions.

These materials are also used in the production of varistors, gas sensors, ultrasonic transducers, and surface-acoustic-wave (SAW) devices due to their high piezoelectricity.[2] Similar to the optical properties, the electrical ones strongly depend on the density and microstructure uniformity.[1,14] The properties of ZnO varistors have, for instance, been reported to be highly influenced by the proportion of grain boundaries.[15,16] Kiselev *et al.*[16] have shown that if the value of the grain-boundary depletion length is fixed, increasing the grain size can reduce the conduction nonlinearity. Duran and colleagues[1,15] have reported that a breakdown voltage for the varistors increases on decreasing the grain size.

ZnO is an excellent model material for investigation of the sintering process. It has a simple structure capable of obtaining a high density by compaction and subsequent sintering at temperatures up to 1300°C without the occurrence of a phase transformation during sintering.[17] Numerous studies have therefore addressed the sintering and growth of the nanocrystalline ZnO grains in recent years.[13,18–21] Gupta and Coble[22] obtained a final density of 97% of theoretical density (TD) and a grain size of ~9 μm at 1200°C by pressureless sintering of pure ZnO powders. Senda and Bradt[23,24] sintered pure ZnO and obtained up to 98% TD at 1100°C. They also reported that addition of Bi_2O_3 increases the ZnO grain size. For the 100 nm undoped ZnO powder, Chu *et al.*[25] obtained 98% TD with a final grain size of 5–10 μm at 1050°C. Kim *et al.*[26] achieved a lower density of 95% TD with initial and final grain sizes of 0.7 and <10 μm at 1000°C, respectively. Han *et al.*[17] sintered a 260 nm powder of pure ZnO and obtained a density of >95% TD with a final grain size of 5 μm at >1100°C. Hynes *et al.*[18] sintered undoped nanophase ZnO (25 nm) to 95%–98% TD at low temperatures (650°–700°C) using pressureless isothermal sintering.

Researchers have recently focused on the application of microwave sintering for fabrication of ZnO compacts.[27–29] With an ultra-high heating rate (up to ~82°C/s), Xu *et al.*[27] have reported that microwave sintering of undoped 1 μm ZnO powder provides an almost fully densified structure with a final grain size of ~4 μm. At least 900°C is required to attain a high density for pure ZnO materials in microwave-sintered ZnO.[28,29] Roy *et al.*[20] sintered two initial particle sizes of 30 and 100 nm at 800°C for 18 ks. The results showed that 30 nm powder compacts densified to 99% TD, while the 100 nm powder compacts only attained a maximum density of 88% TD. Gao and colleagues[2,4] could achieve nanostructured, closed to fully dense (98% TD) ZnO compacts using SPS. This method has yielded such benefits as a rapid sintering rate, high densification, and fine grain size production. It is, however, hardly accessible and scarcely used for practical applications.

Chen and Wang[30] have developed a new technique called two-step sintering (TSS) for Y_2O_3, which is a promising approach to obtain fully dense nanograin ceramics. The key elements in this method reported by Wang and colleagues[31,32] contain: (i) reaching a higher temperature (T_1) to conduct first-step sintering, (ii) achieving a critical density of $\rho^* \geq 75\%$ TD to render pores unstable, and (iii) lowering the temperature to T_2 to conduct second-step sintering during which there is only densification and no grain growth. In addition to Y_2O_3, TSS has been successfully applied to the sintering of Ni–Cu–Zn ferrite,[32] $BaTiO_3$,[32,33] Al_2O_3,[34,35] and liquid-phase sintering of SiC[36] as well as doped ZnO varistors.[1,15]

The influence of step I and step II temperatures deserves, however, to be clarified further. One can emphasize on the significance of these temperatures by considering the technological need for highly densified nanostructured materials of extremely fine grains. The effects of these temperatures on the density and

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