Journal of the European Ceramic Society 36 (2016) 1207–1220

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

FAST/SPS sintering of nanocrystalline zinc oxide—Part I: Enhanced densification and formation of hydrogen-related defects in presence of adsorbed water

Benjamin Dargatz[a,e,*], Jesus Gonzalez-Julian[a], Martin Bram[a], Peter Jakes[b], Astrid Besmehn[c], Lisa Schade[d], Robert Röder[d], Carsten Ronning[d], Olivier Guillon[a]

[a] Institute of Energy and Climate Research, IEK-1, Materials Synthesis and Processing, Forschungszentrum Jülich, 52425 Jülich, Germany
[b] Institute of Energy and Climate Research, IEK-9, Fundamental Electrochemistry, Forschungszentrum Jülich, 52425 Jülich, Germany
[c] Central Institute for Engineering, ZEA-3, Electronics and Analytics, Forschungszentrum Jülich, 52425 Jülich, Germany
[d] Institute of Solid State Physics, Friedrich-Schiller-University of Jena, 07743 Jena, Germany
[e] Otto Schott Institute of Materials Research (OSIM), Friedrich-Schiller-University of Jena, 07743 Jena, Germany

ARTICLE INFO

Article history:
Received 30 September 2015
Received in revised form 6 December 2015
Accepted 11 December 2015
Available online 21 December 2015

Keywords:
FAST/SPS sintering
Nano-crystalline zinc oxide
Adsorbed water
Hydroxide
Defects

ABSTRACT

This part is focused on the effect of surface bound water on the densification behavior and defect stoichiometry of zinc oxide. The second part [doi: 10.1016/j.jeurceramsoc.2015.12.008] concentrates on the effect of hydroxide complexions on the microstructural development, texture formation and anisotropic grain morphology. Nanocrystalline zinc oxide powder was humidified or dried followed by quick heating (100 K/min) with field-assisted sintering technique/spark plasma sintering (FAST/SPS). Densification is strongly enhanced due to hydroxide-ion-diffusion mechanism, which shows species with lower valence and ionic radius in comparison to oxygen ions. The lowered activation energy for densification exhibits no impact of the sintering electric current on this enhanced densification behavior. The defect stoichiometry and structure of sintered zinc oxide was analyzed by several spectroscopic methods, indicating the formation of hydrogen-related defects for sintering in presence of bound water, while no hydrogen was detected for sintering of dried powder.

1. Introduction

Zinc oxide (ZnO) is an interesting and widely investigated material for electrical and optical application, due to its unique combination of physical properties like gas sensitivity, (piezo-) electrical and optical behavior [1–3]. However, materials and industrial application requires well defined device properties. In this context, interface engineering gains increasing impact especially for nanostructured polycrystalline materials, as their high grain boundary area determines the sintering behavior and the final physical properties. Thus, understanding of defect formation during synthesis is essential. During the sintering of oxides several factors affect the oxygen vacancy density such as the reducing/oxidizing atmospheres [4], temperature-history [5], doping [6] or impurities [7]. Interestingly, water is known to adsorb on oxide particle surfaces resulting into a consequent reduction of the surface energy with increasing water layer thickness [8]. Adsorbed water on the surface of nanoparticles is suggested to suppress densification during sintering [9], but recent reports on nanocrystalline ZnO show the opposite behavior [10]. Indeed, the effect of water vapor on the densification of oxides was investigated by some groups [11–16] in the last decades, although the observed phenomena are still unclear. Typically, some oxides do not densify with increasing water vapor pressure, e.g. magnesia (MgO) [12] and tin dioxide (SnO_2) [16]. Moreover, in absence of water anhydrous synthesized MgO nanoparticles could be densified at much lower temperatures than usual [13]. Quach et al. [9] related the hydration of oxide particles to a decrease in driving force due to reduced surface energy, whereas other authors [11,12,16] only discuss kinetic aspects during sintering. Interestingly, Varela et al. [11] observed an increased surface diffusion for ZnO and MgO in presence of water vapor, which contributes to neck formation but not densification. In this context, zinc oxide was identified to exhibit a high potential for interface engineering by means of bound water because of the comparatively low temperature required

---

* Corresponding author at: Institute of Energy and Climate Research, IEK-1, Materials Synthesis and Processing, Forschungszentrum Jülich, 52425 Jülich, Germany.
E-mail address: b.dargatz@fz-juelich.de (B. Dargatz).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.12.009
0955-2219/

for sintering. This behavior was also found at the initial stage of sintering for titania [15]. However, the effect of water vapor on the densification is typically not investigated. Here, high heating rates are required in order to achieve temperatures for densification while the water is still present and affects the surface diffusion process [10]. Such high heating rates can be achieved by field-assisted sintering technology/spark-plasma-sintering (FAST/SPS). Zinc oxide strongly adsorbs water and carbon dioxide molecules on the surface, which is inevitable in ambient atmosphere or even under argon atmosphere within a glovebox [17]. Moreover, it was shown that pre-adsorbed CO_2 can be replaced by H_2O, but CO_2 will remain adsorbed up to 800 °C [17]. Further dissociation of water on the nanocrystal surface might result into hydrogen doping of ZnO. Hydrogen is dopant (or impurity) [18] significantly modifying the oxides electrical properties [18]. Theoretical [19] and experimental [20] works showed that hydrogen is a shallow donor in ZnO, when it is incorporated on interstitial or oxygen vacancy sites [21]. Oba et al. [22] and McCluskey et al. [23] reviewed comprehensively ZnO defects, where hydrogen impurities are most likely to occur at an interstitial site bonded to an oxygen ion with a bond length similar to those in the water molecule. Moreover, theoretical calculations reveal that hydrogen exhibits an energetically preferred interstitial position when surrounded by oxygen vacancies [24]. Here, typically used measurement techniques like electron-spin-resonance spectroscopy [25], photoluminescence spectroscopy [26], solid state NMR spectroscopy [27], electron-energy-loss spectroscopy [28], Raman spectroscopy [29] and infrared spectroscopy [30] are applied to properly characterize the occurrence of hydrogen related defects in ZnO [31]. However, this remained challenging because protons propagate easily already at low temperatures ~100 °C [32]. The overarching goal of the present study is to enable advanced sintering behavior with enhancement of densification, whereas the interaction of water at the interface is especially considered.

2. Experimental procedure

2.1. ZnO materials and powder treatment

Commercial ZnO powder (NG20, Nanogate AG, Quierschied-Göttelborn, Germany) with a purity of >99.99 wt% and a primary particle size between 20 nm and 50 nm was used as starting material. The ZnO powder was dried or humidified just before the sintering process. For the dry process the powder was kept in a drying cabinet for 24 h at 120 °C with «0.5 g/m^3 of water («0.1% relative humidity), while the powder was stored inside a glass beaker within an environmental chamber (KBF 240, Binder GmbH, Tuttlingen, Germany) for 24 h at 20 °C with 14 g/m^3 of moisture for the humidified process. After the storage, the humidified or dried powder was filled in a graphite die, which was hermetically sealed in a freezer bag and compacted for 1 min at 50 MPa by uniaxial pressure. Alternatively, humidification of ZnO powder was realized by addition of deionized water to the pre-pressed green body (16 MPa) with a micropipette directly before sintering. The amount of water added to the green body is defined by the mass fraction $\omega = m_{H_2O}/\left(m_{H_2O} + m_{ZnO}\right)$ and further referred to aqueous condition.

2.2. Field-assisted sintering study

The sintering was performed by field-assisted sintering technology/spark plasma sintering (FAST/SPS) device (HP-D5, FCT Systeme, Rauenstein, Germany) using standard graphite dies with 20 mm inner diameter. A graphite foil of 0.4 mm thickness was placed in the inner face of the die and between the powder and punches in order to prevent fusing of the ceramic material with the graphite during sintering, but to increase the electrical contact. The outer side of the graphite die was covered with graphite insulation in order to reduce the heat loss. The chamber was purged with argon (99.999% purity) and evacuated twice to eliminate the moisture prior to the sintering process. A constant uniaxial pressure of 50 MPa was applied during the whole temperature cycle. The standard heating rate was set with 100 K/min up to maximum sintering temperatures of 400 °C and 800 °C for humid and dry condition, respectively. The temperature was controlled by a thermocouple (type K), which was placed in a radial hole with a distance of 5 mm to the green compact. Densification curves of ZnO were acquired using axial displacement and subsequently corrected subtracting the thermal expansion of the graphite tool, which was performed by the sintering of a dense ZnO with the same thermal cycle.

Moreover, the effect of an electrical current during sintering on the densification behavior of humidified zinc oxide was investigated in further experiments. Therefore, electrically insulating high density alumina plates were inserted between the ceramic body and the graphite stamps, which is illustrated elsewhere [33]. The data sheet of these alumina plates (Rubalit 710 Alumina, CeramTec GmbH, Plochingen, Germany) announces an electrical resistance of 10^{13} Ωcm and 10^9 Ωcm at 20 °C and 900 °C, respectively. Thus, electrical current through the zinc oxide body is blocked.

2.3. Free sintering under constant atmosphere in redox-furnace

A free sintering study on nanocrystalline zinc oxide (NG20) at defined atmosphere was performed by means of a redox-furnace (RS 120/750/11, Nabertherm GmbH, Lilienthal, Germany). The redox furnace consists of an alumina tube inside a quartz glass tube, which was sealed and flushed with a constant gas flux of 200 ml/min at ambient gas pressure. Either dry argon gas (99.999%) or dry argon/hydrogen (2 vol%) was used. Further humidification of the gas in boiling water enabled to set defined reducing or oxidizing atmospheres. The gas moisture was measured by a humidity sensor and the volume fraction of water vapor was controlled by water temperature and finally set to 10 vol%. The ZnO NG20 powder was dry pressed to a green density of 43% of theoretical density (TD) with 20 mm diameter and 4 mm height and finally placed in the center of the tube on an alumina plate. The tube was flushed for one hour with the set gas mixture before each sintering run in order to prevent the contamination. In the following, the temperature was raised with 10 K/min up to a temperature of 700 °C or 800 °C with isothermal sintering times between 30 and 90 min. The temperature was controlled by a type K thermocouple located at a distance of 5 mm from the specimen.

2.4. Investigation of electrical properties and defect structure

2.4.1. Impedance spectroscopy

The impedance spectroscopy (IS) was performed on bars ($1.5 \times 1.4 \times 18$ mm^3), which were cut out from the sintered specimen. The front faces of the bar were coated with gold in a sputter coater for 3 min and electrically contacted afterwards with silver paste on a silver wire. The adhesion of the silver paste was warranted by drying in an oven at 65 °C for 24 h. The measurements were carried out in ambient atmosphere within a temperature test chamber (VT4002 EMC, Vötsch Industrietechnik GmbH, Balingen-Frommern, Germany) in a temperature range between −30 °C and 90 °C with an interval of 10 K. The specimens were kept for 45 min at a constant temperature before the electrical measurements were performed. The impedance spectra were collected by an impedance analyzer (VMP-300 built-in EIS Analyzer, BioLogic, Claix, France). Results are given as a mean value of five successive separate measurements in a frequency range between 1 Hz and 7 MHz with