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Effect of Al and Mn doping on the electrical conductivity of ZnO

Jiaping Han, P.Q. Mantas *, A.M.R. Senos

Department of Ceramic and Glass Engineering/UIMC, University of Aveiro, 3810-193 Aveiro, Portugal

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Abstract

Samples of Al-doped and Mn-doped ZnO with a doping level up to 1.2 mol% were sintered at temperatures from 1100 to 1400°C in air. dc Electrical conductivities of these samples at room temperature and below were measured, and the effects of the doping type, the doping level, the sintering temperature and time on the electrical conductivity of ZnO were investigated. It was found that Al increased the electrical conductivity of ZnO resulting in a manifestation of a metallic electrical conduction behaviour, and a semiconductor-metal transition occured in the Al-doped ZnO samples. For Mn-doped ZnO samples quenched from the sintering temperatures, the electrical conductivity decreased with the increase in the Mn content, but the samples still showed a semiconductor electrical conduction behaviour. In this way, one could obtain a systematic variation of the ZnO electrical conductivity from the high conductivity, Al-doped case, to the high resistivity, Mn-doped one, spanning over eight orders of magnitude, which is explained in the present communication. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical conductivity; Impurities; Sintering; ZnO

1. Introduction

A typical ZnO based varistor is a very complex chemical system and contains several dopants, such as Bi, Mn, Co, Sb, Al, and Cr.[1,2] The varistor behaviour of ZnO ceramics is directly related to the composition and to the microstructural development.[1–4] Therefore, it is important to understand the effect of the individual additives both on the electrical properties and on the microstructural development of ZnO.

The effect of Al doping on the electrical properties of multicomponent ZnO varistors has been investigated by several researchers[5,6] It has been observed that Al increases the high current conductivity in the upturn region of ZnO varistor and delays the onset of voltage upturn to higher current density. In this way, the region of nonlinearity of ZnO varistors can be extended to higher applied fields. Since the conductivity in the upturn region depends on the grain conductivity of ZnO, it is expected that Al increased the conductivity of the ZnO grains. A systematic study of the effect of Al doping on the conductivity of ZnO is, therefore, necessary. The effect of Mn doping on the electrical properties of ZnO varistor has also been investigated in multicomponent systems,[7–9] and it is generally accepted that Mn can significantly improve the nonlinear current-voltage characteristics of ZnO varistors by affecting the defect chemistry at the grain boundaries. However, the effect of Mn on the grain conductivity of ZnO is still unclear.

The effects of individual additives, such as Al and Mn, on multicomponent ZnO varistors are complicated by other additives. Hence, it is necessary to address the various additives independently in a systematic way to achieve an understanding of the roles of these additives. In our previous works,[10–12] the effects of Al and Mn on the densification and grain growth of ZnO were investigated in two simple binary systems of Al-doped ZnO and Mn-doped ZnO. It was observed that Al doping significantly inhibited the grain growth and reduced the driving force for sintering by forming a second phase,[10] while Mn reduced the densification rate in the early stage of sintering[11] and promoted the grain growth of ZnO in the intermediate and final stage of sintering.[12] In this work, the effects of Al and Mn on the electrical conductivity of ZnO were investigated in samples sintered from 1100 to 1400°C in two binary systems, Al-doped ZnO and Mn-doped ZnO.

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* Corresponding author. Tel.: +351-234-370261; fax: +351-234-425300.

E-mail address: pmantas@cv.ua.pt (P.Q. Mantas).

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2. Experimental procedure

Reagent grade ZnO powder (Aldrich, Milwaukee, WI) with 99.9% purity and a mean particle size of 0.26 μm was used. To dope with Al and Mn, ethanol based solutions of hydrated aluminium nitrate ($Al(NO)_3 \cdot 9H_2O$) and of hydrated manganese nitrate ($Mn(NO_3)_2 \cdot 4H_2O$) were prepared and mixed with ZnO powder in a planetary milling for 4 h. The slurries were dried, and the obtained powders were calcined at 450°C for 1 h. Disk-shaped specimens of 10 mm diameter and 1–2 mm height were obtained by uniaxial pressing at 100 MPa, followed by isostatic pressing at 200 MPa. The temperature of a tubular furnace was raised up to a predetermined value. Samples were quickly inserted in the centre of the furnace. After being sintered for a predetermined time, the samples were quenched to room temperature in air.

Sintered samples were polished with 1200-grit SiC on both sides, ultrasonically cleaned, and then vacuum deposited with gold electrodes or covered with In–Ga electrodes. dc Electrical conductivity was measured with an electrometer (Model 617, Keithley, USA) and a multimeter (Model 197, Keithley, USA). No nonlinear I–V behaviour was observed in all the samples with the measuring voltage up to 100 V or the measuring current up to 10^{-2} A. Low temperature measurements were performed in a cryogenic system (Model HC-2, APD Cryogenics Inc., USA). Temperature control and measurements were performed with a microprocessor cryogenic temperature controller (Model 9650, Scientific Instruments Inc., USA). All data were reproducible within the experimental error.

3. Results and discussion

3.1. *Effect of Al on the electrical conductivity of ZnO*

Fig. 1 shows the room temperature dc electrical conductivity of the sintered samples of undoped and Al-doped ZnO as a function of the sintering temperature for 2 h. For 1100°C, the conductivity decreased with the increase in the Al content, and for low Al content, i.e. 0.08 and 0.32 mol% Al, the conductivity is higher than the undoped one, but for higher Al content, it is smaller than the undoped one. When the sintering temperature was increased from 1100 to 1200°C and more, the conductivity of Al-doped ZnO increased significantly and became considerably higher than the undoped one, and the difference of the conductivities of ZnO with different Al doping levels became very small. It was observed in our previous work[10] that the densities of Al-doped ZnO at 1100°C were much lower than those at higher temperatures and also decreased with increasing Al content. The existence of a large amount of pores may be the main reason for the significant decrease of conductivity in Al-doped ZnO at 1100°C, especially for the higher Al doping levels. However, with increasing the sintering temperature from 1100 to 1200°C and more, the density of Al-doped ZnO significantly increased, and the solid solution of Al in ZnO may become the main influencing factor on the conductivity of ZnO. It is known[5,6] that the trivalent aluminium ion dissolved in ZnO acts as a shallow donor, and should increase the conductivity of ZnO. This is in agreement with the experimental observation that the Al-doped samples have considerably higher conductivities for 1200–1400°C, compared with the undoped one. However, the conductivity was not further increased and was kept almost constant with increasing the Al doping level. The possible reason for this phenomenon is that all the doping levels in this work probably exceeded the solid solubility of Al in ZnO, which was determined to be ~0.06 mol% at 1200C in our previous work.[10]

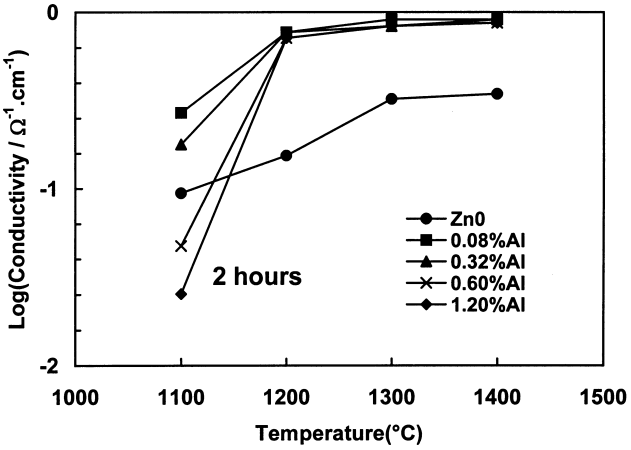

Fig. 1. Room temperature dc electrical conductivity of the sintered samples of undoped and Al-doped ZnO as a function of the sintering temperature for 2 h.

Fig. 2 shows the room temperature dc electrical conductivity of the sintered samples of undoped and Al-

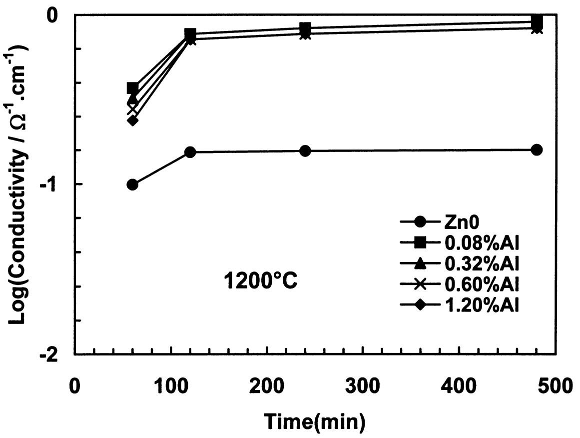

Fig. 2. Room temperature dc electrical conductivity of the sintered samples of undoped and Al-doped ZnO as a function of the sintering time at 1200°C.

doped ZnO as a function of the sintering time at 1200°C. For Al-doped ZnO, the conductivity increased obviously with increasing the sintering time from 1 h to 2 hours, but with further increases of sintering time it changed slightly. On the other hand, Al doping increased markedly the conductivity of ZnO, but no significant effect of Al doping level from 0.08 to 1.2 mol% on the conductivity of ZnO was observed. Our previous work[10] showed that the density of Al-doped ZnO increased with the increase in the sintering time at 1200°C. The densities of Al-doped samples sintered for 1 h were relatively low, and the influence of pores on the conductivity may be considerable, while sintering for longer times gave higher densities, and the solid solution of Al in ZnO is probably dominating the conductivity. Therefore, the results in Fig. 2 are explained similarly to those of Fig. 1.

Fig. 3 illustrates the temperature dependence of the dc electrical conductivity of the sintered samples, from 10 to 300 K. Clearly, the undoped ZnO showed a typical semiconductor behaviour, i.e. with increasing the temperature, the conductivity significantly increased in the low temperature range ($<\sim$120 K), and then increased slightly in the high temperature range ($>\sim$120 K). An activation energy of ~0.04 eV can be determined from this temperature dependence in the low temperature range. However, the conductivity of ZnO doped with 0.08 mol% Al kept almost constant in the entire temperature range, 10–300 K, which means that the effective ionisation energy of the shallow donor in this sample vanishes, i.e. the material showed a metallic type behaviour. The same temperature dependence of the conductivity was found in the other Al-doped samples, i.e. ZnO doped with 0.32, 0.60 and 1.20 mol% Al (for the sake of clarity, Fig. 3 does not show the curves for these samples). Al dissolved in ZnO substitutes Zn and forms a weakly bound electron. The overlapping of the wave functions of these weakly bound electrons forms an impurity band in the band gap. The higher the density of the electrons, the broader the impurity band. When the Al doping level is very high, the impurity band will become broad enough to reach the edge of the conduction band. As a result, the effective ionisation energy of these shallow donors becomes zero. The critical donor concentration at which this semiconductor-metal transition is expected to occurs in ZnO can be calculated from various theoretical models,[13] changing from 4.8×10^{18} to 2.2×10^{19} cm^{-3} (i.e. from ~0.01 to ~0.05 mol%) depending on the chosen theoretical model.[14] In the present work, the actual Al concentrations dissolved in ZnO, even considering the solubility of Al in ZnO, are beyond these theoretical critical donor concentrations. Hence, an expected semiconductor-metal transition occurred in these Al-doped samples, supporting the observed metallic type conduction behaviour.

2.2. *Effect of Mn doping on the electrical conductivity of ZnO*

Fig. 4 shows the room temperature d.c. electrical conductivity of the samples as a function of the Mn concentration in the samples sintered at different temperatures for 2 h. It can be observed that the conductivity decreased with the increase in the Mn concentration and increased with increasing the sintering temperature, especially at 1100C. Mn doping reduced markedly the conductivity from ~10^{-1} Ω^{-1} cm^{-1}, for undoped ZnO, to ~10^{-8} Ω^{-1} cm^{-1}, for 0.6 mol% Mn doped ZnO. The relative densities of all the sintered samples of undoped and Mn-doped ZnO were in the range of 92%–96%, and no significant effect of Mn doping on the sintered density was observed, as shown in a previous work.[12] Moreover, no second phase was found in these samples by XRD, SEM, or TEM analyses. Therefore, other factors rather than the den-

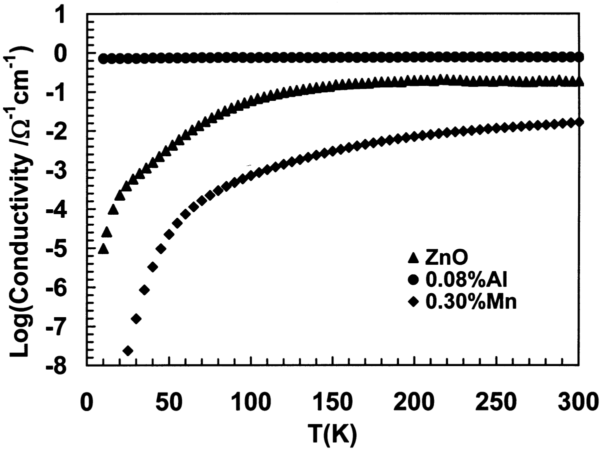

Fig. 3. Temperature dependence of the dc electrical conductivity of the sintered samples.

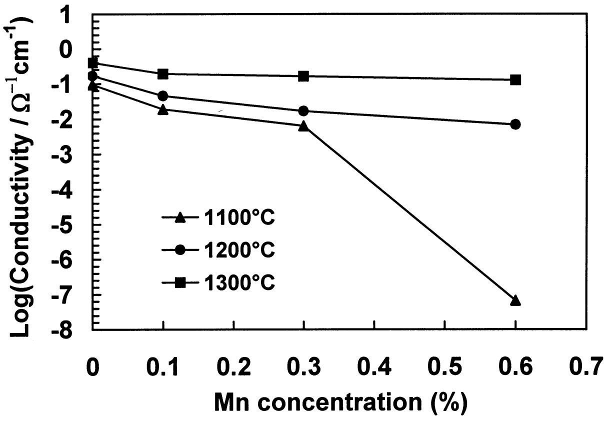

Fig. 4. Room temperature dc electrical conductivity of the samples as a function of the Mn concentration in the samples sintered at different temperatures for 2 h.

sity or the presence of a second phase should be responsible for the reduction of the conductivity due to Mn doping. We found that all the samples in this work showed linear electrical current-voltage behaviour, which indicates that electrical barriers are not formed in these samples. Furthermore, Fig. 3 shows that the temperature dependence of the dc electrical conductivity of the 0.3 mol% Mn doped ZnO sample is similar to the undoped one, i.e. it shows a typical semiconductor characteristic. Similar behaviour can also be observed in the other Mn-doped samples. It seems that Mn affects the bulk conductivity of ZnO probably by affecting the defect chemistry of the bulk ZnO. The defect equilibra of undoped and Mn-doped ZnO at the sintering temperatures were therefore calculated. The detailed calculation procedure will be presented in a forthcoming publication. The results showed that when Mn is dissolved in ZnO, it behaves as a deep donor and depresses the concentrations of the intrinsic donors at the sintering temperatures. When the samples are quenched from the sintering temperatures to room temperature, as is the case in the present work, the concentrations of the intrinsic donors at room temperature are also lowered, since they are equal to the concentrations at the sintering temperature due to the fast freezing process. In this way, the room temperature electrical conductivity, mainly arising from the ionisation of the intrinsic donors, is lowered by the presence of Mn. However, the Mn doping does not give a direct contribution to the room temperature conductivity of ZnO, because the Mn deep donors can not be ionised at room temperature due to their high ionisation energy (~2.0 eV). On the other hand, with increasing the sintering temperature, the concentrations of the native defects, namely the intrinsic donor defects, increase, which results in the increase of the room temperature electrical conductivity as shown in Fig. 4.

4. Conclusion

The effects of Al and Mn doping on the electrical conductivity of ZnO were investigated in two simple binary systems of Al-doped and Mn-doped ZnO. It was found that Al increased the electrical conductivity of ZnO probably by forming a shallow donor in ZnO. The Al doping level in this work is high enough to exceed the theoretical critical donor concentration at which a semiconductor-metal transition is expected to occur. This transition is confirmed by the disappearance of a conduction activation energy in these Al-doped ZnO samples. On the other hand, it was observed that Mn reduced the electrical conductivity of ZnO in the samples quenched from the sintering temperatures, but these samples still showed a semiconductor electrical conduction behaviour. The defect equilibra calculations, presented in another work, showed that Mn dissolved in ZnO behaved as a deep donor and depressed the concentrations of the intrinsic donors at the sintering temperatures. As a result, these concentrations at room temperature were also lowered due to fast freezing of the ionic defects during quenching. In this way, the room temperature electrical conductivity, mainly arising from the ionisation of the intrinsic donors, is lowered by the presence of Mn.

Acknowledgements

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