J Mater Sci: Mater Electron **(2023) 34:82**

Low-temperature sintering of ZnO:Al ceramics by means of chemical vapor transport

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Received: 21 July 2022
Accepted: 30 October 2022

ABSTRACT

A new technological approach for sintering Al-doped ZnO ceramics using chemical vapor transport (CVT) based on HCl has been developed. Among the advantages of the proposed sintering approach are: the low sintering temperature of 1070 °C; the absence of deviation in the diameter of ceramics after sintering; and the presence of Zn excess in the resulting material. The influence of dopant powder, concentration of Al, powder compacting pressure, and stoichiometric deviation on the density and conductive properties of ceramics has been investigated. Due to the relatively weak interaction of Al_2O_3 with HCl and limited solubility of Al in ZnO, a doping level about 2 at.% is recommended. A further increase in the dopant concentration significantly reduces the density and conductivity of the resulting material. A theoretical and experimental comparative analysis of the features of CVT sintering of ZnO doped with Al, Ga, and In was also carried out. ZnO:Al:Cl CVT ceramics with the resistivity of $9.5 \times 10^{-3}\ \Omega$ cm can be used as stable magnetron targets for ZnO thin films deposition with improved conductive properties. The influence of dopant powder, Al concentration, deposition temperature, and the gaseous medium of sintering target on the electrical properties of films are investigated and discussed.

1 Introduction

ZnO thin films have shown broad prospects for various application, such as transparent electrodes in solar cells, light emitting diodes, gas sensors, and piezoelectric transducers [1]. One of the simplest and controllable methods for deposition of conductive thin films is magnetron sputtering [1]. Usually, several type of targets are used for deposition, such as Zn targets partially coated with Al [2], Zn + Al alloy targets [2], ZnO:Al_2O_3 ceramic targets [3–6], as well as co-sputtering of ZnO and Al targets [7]. The sputtering of Al-doped ZnO ceramics proved to be the most controllable technique among them. The commonly used sintering method of ceramic targets consists in compacting an initial powder with

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https://doi.org/10.1007/s10854-022-09458-1

subsequent annealing in air. This method has several disadvantages [3–6], including (i) the necessity to use a high-pressure technology (up to 100 MPa) for the compacting of initial powder; (ii) high sintering temperatures (1300−1500 °C) which are required to obtain materials with a fairly high density, hardness, conductivity and uniform doping; (iii) a change in the diameter of the ceramics during sintering; (iv) uncontrollable stoichiometric deviation. One of the most conductive and dense ZnO:Al ceramics with a resistivity of 2.3×10^{-3} Ω cm and a density of 5.6 g/cm^3 was obtained by sintering ZnO:Al nanopowder (particle size 20−30 nm) prepared through co-precipitation method [3]. The solubility limit of Al in ZnO ceramics and films is about 2−3 at.%. A higher doping level leads to a deterioration in uniformity of ceramics and conductive properties of thin films [6].

Recently, chemical vapor transport (CVT) technique based on HCl, successfully developed for ZnO single crystal growth [8], was proposed as an alternative approach for sintering ZnO:Cl ceramics with a controllable stoichiometric deviation [9]. This approach does not require the use of doped ZnO nanopowders and powder compacting at high pressure, change in the diameter of the ceramics after sintering was not observed. The CVT sintering also gives the possibility of multiple re-sintering and an essential decrease in the sintering temperature to 1000 °C−1070 °C. The low sintering temperature is related to an effective interaction between ZnO and HCl; a high pressure of gaseous species involved in CVT reactions ($ZnCl_2$ and H_2O vapors) can contribute to the formation of ceramics in the gas phase even at low temperatures [9, 10]. Some oxides effectively interact with the CVT gaseous medium generating highly volatile chlorides. This effect leads to an increase in the dissolution rate of the corresponding dopants by several orders of magnitude. Highly conductive and uniformly doped ZnO:Ga:Cl ceramics were successfully synthesized at a temperature as low as 1070 °C [10].

Al is the most typical and cost effective dopant for ZnO; ZnO:Al thin films have prospects for application in photoconductive devices [1]. The typical value of resistivity for ZnO:Al thin films deposited using the magnetron sputtering technique is about $(0.5–2) \times 10^{-3}$ Ω cm [3, 6, 11]. Al-doping efficiency in ZnO (fraction of Al atoms acting as shallow donors) is relatively low; being only 4% for films having 50 nm thickness and increases to about 15% for the film thicknesses more than 450 nm (3 at.% Al). Al dopant creates charge traps and homologous phases, especially in very thin films at high doping level [12]. Up to now, several methods were reported, aimed to increase the conductivity of ZnO thin films, such as ultraviolet stimulation of growing films [13], binary doping with metallic impurities [3], rapid thermal annealing [14], an increase in the magnetic field strength [15], the use of ZnO:Ga buffer layer [16], excess of Zn or carbon in ceramics generating additional intrinsic donor defects such as oxygen vacancies (V_O) [17], co-doping with hydrogen, which contributes to a higher concentration of V_O donors [18] and a formation of metal impurity−H−O shallow donor defects [19].

Co-doping with III-valence metals and halogens is one of the most promising approaches to improve the Al-doping efficiency and conductive properties of ZnO:Al films. A decrease in the resistivity by 2 times to 2.9×10^{-4} Ω·cm (350 nm film thickness, 200 °C temperature deposition) was reported for ZnO:Al:F thin films, compared to simple doping with Al [11]. At the same time, similar films with improved conductive properties were obtained by co-doping with Ga + F [20] and Ga + Cl [21]. The additional halogen impurity contributes to a better incorporation of the metal impurity into the ZnO lattice as shallow donors [10, 21]. This effect can be explained by the chemical interaction of halogens and the main (metal) impurity atoms. The volatile halides (AlF_3, GaF_3, $GaCl_3$) resulting from this interaction should have a significantly higher mobility and surface migration length compared to the corresponding oxides. The metal atoms bounded with halogens have a higher probability to be incorporated into the ZnO lattice as shallow donors [21].

The goal of this study consist in: (i) the development a new low-temperature sintering technology for Al-doped ZnO ceramics using CVT based on HCl; the resulting ceramic targets sintered in an oxygen-free gas medium should have some stoichiometric deviation (Zn excess), which improves the conductive properties of thin films; (ii) comparative analysis of ZnO CVT ceramics doped with Al, Ga, In; (iii) theoretical and experimental investigation of effect of additional chlorine impurity (interaction between Al and Cl during film deposition) and comparison with other co-doping results.

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