




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

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## 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<sub>2</sub>O<sub>3</sub> 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  $9.5 \times 10^{-3} \Omega \text{ cm}$  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<sub>2</sub>O<sub>3</sub> 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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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  $2.3 \times 10^{-3} \Omega \text{ cm}$  and a density of  $5.6 \text{ g/cm}^3$  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<sub>2</sub> and H<sub>2</sub>O 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  $(0.5\text{--}2) \times 10^{-3} \Omega \text{ cm}$  [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 ( $V_{\text{O}}$ ) [17], co-doping with hydrogen, which contributes to a higher concentration of  $V_{\text{O}}$  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  $2.9 \times 10^{-4} \Omega \cdot \text{cm}$  (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<sub>3</sub>, GaF<sub>3</sub>, GaCl<sub>3</sub>) 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.

## 2 Preliminary thermodynamic notes

The saturated vapor pressure of many oxides is very low. This factor lead to a low dissolution rate of oxide dopants, when ZnO ceramics is sintered at low temperatures (~1000 °C) in air or inert gas atmosphere. The intensive interaction between ZnO and HCl generates ZnCl<sub>2</sub> and H<sub>2</sub>O vapors [8, 22]. ZnCl<sub>2</sub> vapors act as a transport agent (TA) for some oxides, increasing the dissolution rate of the corresponding dopants in ZnO at low-temperature sintering [8, 23]. The main reactions of the ZnO–Al<sub>2</sub>O<sub>3</sub>–HCl CVT system are the following:

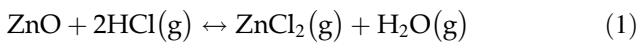


Figure 1a shows the calculated composition of the ZnO–Al<sub>2</sub>O<sub>3</sub>–HCl CVT system, for the initial pressure of HCl (HCl<sup>o</sup>) of 1 atm at the sintering temperature. Examples of thermodynamic calculations are shown in Ref. [23]. The presence of ZnCl<sub>2</sub> and H<sub>2</sub>O vapors promotes sintering ZnO ceramics by means of CVT [9]. The saturated vapor pressure of Al<sub>2</sub>O<sub>3</sub> at 1000 °C is about 10<sup>-32</sup> atm [24]. AlCl<sub>3</sub> vapor pressure is 24 orders of magnitude higher (7.0 × 10<sup>-9</sup> atm at 1000 °C, HCl<sup>o</sup> = 1 atm) in the ZnO–Al<sub>2</sub>O<sub>3</sub>–HCl CVT system. However, this pressure is relatively low for an effective doping with Al. Therefore, Al<sub>2</sub>O<sub>3</sub> nanopowder should be recommended as a dopant for better dissolution in ZnO ceramics. For comparison, GaCl<sub>3</sub> and InCl<sub>3</sub> vapor pressure reaches a value of 1.0 × 10<sup>-3</sup> and 1.4 × 10<sup>-2</sup> atm, respectively, in the ZnO–Ga<sub>2</sub>O<sub>3</sub> (In<sub>2</sub>O<sub>3</sub>)–HCl CVT systems (Fig. 1a, inset).

The main reactions of the ZnO–Al–HCl CVT system are the following:

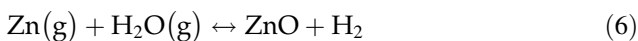
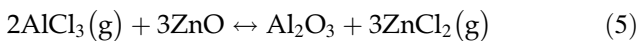
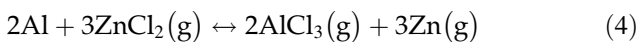
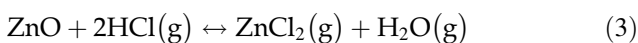
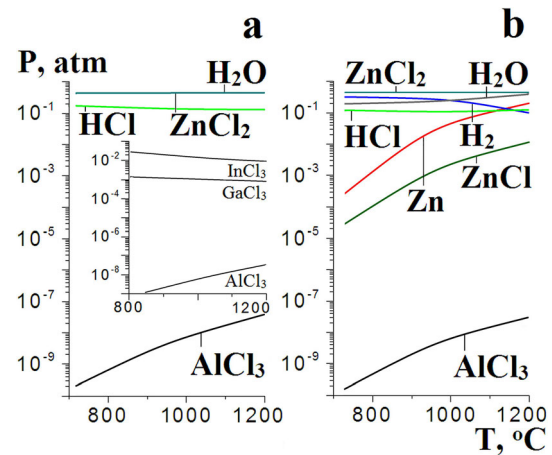


Figure 1b shows the calculated composition of the ZnO–Al–HCl CVT system, for the initial HCl



**Fig. 1** Temperature dependence of composition for **a** ZnO–Al<sub>2</sub>O<sub>3</sub>–HCl and **b** ZnO–Al–HCl CVT systems. HCl<sup>o</sup> = 1 atm, Al<sup>o</sup> = 0.17 atm. Inset illustrates a comparison of MeCl<sub>3</sub> pressures for ZnO–Me<sub>2</sub>O<sub>3</sub>–HCl CVT systems (Me = Al, Ga, In). The composition calculations are based on the thermodynamic data from Refs. [24, 25]

pressure of 1 atm and the loaded quantity of Al corresponding to 0.17 atm at the sintering temperature. Loaded Al should completely transform into gaseous AlCl<sub>3</sub>, which, diffusing and interacting with ZnO particles, should almost completely turn into Al<sub>2</sub>O<sub>3</sub> (Eqs. 4, 5). The equilibrium pressure of AlCl<sub>3</sub> should be relatively low. Zn vapors and H<sub>2</sub> should also be present in this CVT system according to Eqs. 4, 6.

The ZnO–Al<sub>2</sub>O<sub>3</sub>–HCl and ZnO–Al–HCl CVT systems do not contain oxygen. ZnO CVT ceramics should have some Zn excess, intrinsic donor defects, which contributes to a higher free electron concentration and conductivity of thin films [17, 18]. At the same time, the interaction of Al<sub>2</sub>O<sub>3</sub> and ZnCl<sub>2</sub> vapors should be very weak at the low temperatures typical for magnetron sputtering deposition (100 °C–300 °C). The corresponding calculation shows that the equilibrium (thermodynamic) fraction of Cl atoms bound with Al impurity atoms on the surface of growing ZnO films is as low as 7.5 × 10<sup>-25</sup> at temperature of 120 °C, ZnCl<sub>2</sub> and Zn vapor pressure of 10<sup>-8</sup> atm, and Al concentration of 2 at.%. For comparison, under the same conditions, the fraction of Cl atoms bound with Ga and In impurity atoms should reach values of 0.22 and 0.99, respectively.

Thus, HCl can be a promising TA for the low-temperature sintering ZnO:Al ceramics. However,

the interaction of  $\text{Al}_2\text{O}_3$  with the gaseous medium should be relatively weak. Therefore,  $\text{Al}_2\text{O}_3$  nanopowder or metallic Al powder should be recommended as dopants. The ZnO:Al:Cl CVT ceramics should have some stoichiometric deviation, which contributes to a higher charge carrier concentration of thin films. At the same time, the reaction of  $\text{Al}_2\text{O}_3 + \text{ZnCl}_2$  should be weak at low temperatures typical for magnetron sputtering; consequently, the effect of the residual Cl impurity on the conductive properties of ZnO films can be relatively low.

### 3 Experiment

ZnO:Al:Cl ceramics were sintered in sealed quartz chambers at 1070 °C for 48 h. A ZnO +  $\text{Al}_2\text{O}_3$  or ZnO + Al mixed powder was loaded onto the flat bottom of chambers. For many experiments, powder compacting with a low pressure of 5 atm was applied. Several comparative experiments were also carried out with compacting at a higher pressure of 90 and 150 atm. Before loading TA, the sintering chamber (material) was purified by annealing in a dynamic vacuum of  $10^{-5}$  atm for 10 min. The technological details of sintering were described in details in Ref. [9]. A ZnO powder (99.98%) with a particles size of 30–100  $\mu\text{m}$  was used as the source material. Three types of powders were used as dopant: (i)  $\text{Al}_2\text{O}_3$  (99.5%) micropowder with a particles size of 50–100  $\mu\text{m}$ ; (ii)  $\text{Al}_2\text{O}_3$  (99.8%) nanopowder with a particles size of 20–50 nm; and (iii) micropowder of Al (99.8%) with a particles size of 20–50  $\mu\text{m}$ . These three types of dopants will be labeled in this work as AOm, AOn, and Am, respectively. The loaded concentration of Al in ceramics ( $[\text{Al}]/([\text{Al}]+[\text{Zn}])$ ) was varied in a range of 0–6 at.%. To change the stoichiometric deviation of the ZnO:Al ceramics, several samples were additionally annealed in air and in saturated Zn vapors (800 °C, 18 h). Several experiments were also carried out for obtaining ZnO:In:Cl CVT ceramics ( $\text{In}_2\text{O}_3$  dopant powder: 99.99%, 20–30  $\mu\text{m}$ , 2–6 at.% In). Hydrogen chloride was used as a TA with a loading pressure of 2 atm at the sintering temperature. The sintered ceramics are characterized by the typical dimension of 2 mm in thickness and 25 mm in diameter.

ZnO:Al:Cl thin films were deposited on glass substrates by DC magnetron sputtering using the synthesized ZnO:Al:Cl ceramic samples as the

targets. With the purpose of comparison, several thin films were deposited using classical ZnO:Al ceramic targets sintered in air or inert gas atmosphere. Argon with a purity of 99.998% and a pressure of  $4 \times 10^{-6}$  atm was used as the working gas. The substrate–target distance and the magnetron power were 5 cm and 10 W, respectively. The deposition temperature was varied in a range of 120 °C–250 °C. The thickness of the deposited ZnO:Al:Cl films was about 600–650 nm. Additional post-growth annealing of films was not performed in any of the cases.

All obtained ceramic samples were purified by annealing in a dynamic vacuum at 300 °C for 30 min, prior to the study of electrical properties. The resistivity ( $\rho$ ), charge carrier concentration ( $n$ ), and Hall mobility ( $\mu$ ) of ceramics and thin films were calculated from the Hall effect measurements by van der Pauw method.  $2\theta$  X-ray diffraction (XRD) spectra, recorded using  $\text{FeK}_\alpha$  radiation (1.936 Å), were used to analyze the crystallinity of the samples. The morphology and chemical composition microanalysis were studied using a TESCAN Vega TS 5130MM scanning electron microscope (SEM) equipped with a back scattered electron (BSE) detector and an Oxford Instruments INCA energy dispersive X-ray analysis system. To evaluate the thermal stability of conductive properties, ZnO:Al:Cl ceramics were annealed in a temperature range of 20 °C–400 °C in a dynamic vacuum for 30 min. The transmittance spectra of the thin films were studied in the 300–1000 nm spectral range. All measurements were carried out at room temperature (25 °C). The standard deviation for values of  $\rho$ , sheet resistance ( $R_s$ ) and average transmittance in a visible spectral range ( $\text{Tr}_{\text{av}}$ ) was 2%. The error bars for graphs containing  $\rho$  values are smaller than the symbols used in plotting the data. The density ( $d$ ) of ceramic samples, figure of merit  $\text{FM} \equiv \text{Tr}_{\text{av}}^{10}/R_s$  of thin films [26], and impurity concentration in ceramics were measured with an error of 10%. The error of other values (hardness ( $H$ ),  $n$ ,  $\mu$  for ceramics and thin films) was 30%.

## 4 Experimental results and discussion

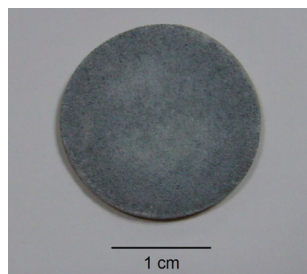
### 4.1 ZnO:Al:Cl ceramics

HCl can be used as an effective TA for the low-temperature sintering of ZnO:Al:Cl ceramics with a diameter of at least 25 mm (Fig. 2). When  $\text{Al}_2\text{O}_3$



micropowder (AOm dopant) is used, the resulting material contains microinclusions with a high Al concentration ( $\sim 12$  at.%) (Fig. 3a). XRD measurements revealed intensive peaks characteristic for ZnO and several peaks related to  $\text{ZnAl}_2\text{O}_4$  spinel phase as seen in Fig. 4a. The intensity of  $\text{ZnAl}_2\text{O}_4$  peaks increases with increasing the doping level (Fig. 4, inset). To provide a better dissolution of  $\text{Al}_2\text{O}_3$  in ZnO, an  $\text{Al}_2\text{O}_3$  nanopowder must be used. As it can be seen from Fig. 4b, the intensity of XRD peaks related to the  $\text{ZnAl}_2\text{O}_4$  spinel phase is 2–3 times lower in the case of AOn dopant. Some residual powder with an average Al concentration of about 12 at.% is observed in SEM images of ZnO ceramics doped by AOn (Fig. 3b, small gray particles). The most uniform material without significant Al,  $\text{Al}_2\text{O}_3$  or  $\text{ZnAl}_2\text{O}_4$  inclusions can be obtained using metallic Al (Fig. 3c). XRD measurements revealed several weak peaks related to the spinel phase in the case of Am dopant (Fig. 4c). It is expected that  $\text{ZnAl}_2\text{O}_4$  is concentrated at the boundaries of ZnO crystallites.

The density and hardness of ZnO ceramics obtained using CVT based on HCl are  $5.1 \text{ g/cm}^3$  (91% relative density) and 2.0 GPa, respectively [9]. The density of ZnO ceramics obtained under the same conditions and doped with Al (2 at.%) is significantly lower, about  $4.0 \text{ g/cm}^3$  (Fig. 5a). The hardness of ZnO:Al:Cl ceramics was found to be also lower, of about 1.1 GPa. Thus,  $\text{Al}_2\text{O}_3$  and  $\text{ZnAl}_2\text{O}_4$  undissolved dopant inclusions slow down the sintering rate of ceramics in the case of ZnO– $\text{Al}_2\text{O}_3$ –HCl CVT systems. Non-equilibrium  $\text{AlCl}_3$  vapors in the ZnO–Al–HCl CVT systems, formed by the interaction of metallic Al and  $\text{ZnCl}_2$ , should interact with ZnO (Eqs. 4, 5). Obviously, in the case of ZnO–Al–HCl CVT systems, the initial ZnO particles are covered with a thin layer of  $\text{Al}_2\text{O}_3$  or  $\text{ZnAl}_2\text{O}_4$ , which suppresses further sintering and reduces the density of the obtained material. The increase in the



**Fig. 2** ZnO:Al:Cl ceramic target (AOn dopant, 2 at.% Al)

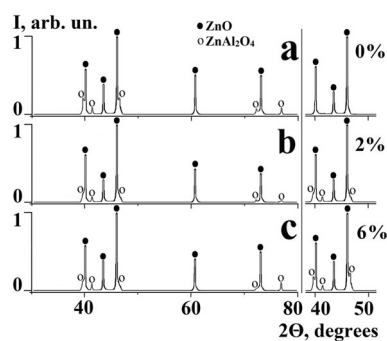
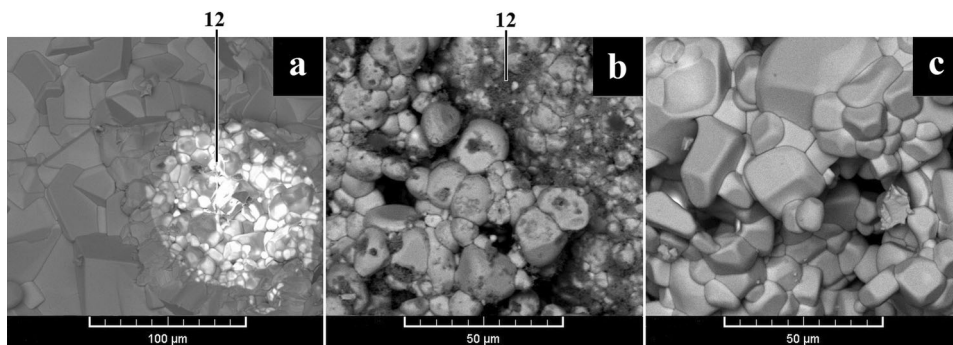
doping level up to 6 at.% significantly reduces the density of the resulting material at any used dopant (Fig. 5a).

The unintentionally doped ZnO:Cl ceramics are characterized by the following electrical parameters:  $\rho = 3.5 \times 10^{-2} \Omega \cdot \text{cm}$ ,  $n = 6 \times 10^{18} \text{ cm}^{-3}$ , and  $\mu = 30 \text{ cm}^2/\text{Vs}$  (Fig. 5, open symbols) [10]. These conductive properties are attributed to the residual Cl impurity (with concentration of about  $4 \times 10^{19} \text{ cm}^{-3}$  [27, 28]) and intrinsic donor defects such as oxygen vacancies. The charge carrier concentration is 2–3 times higher in ZnO:Al:Cl ceramics (2 at.% Al) (Fig. 5c). At the same time, the presence of  $\text{Al}_2\text{O}_3$  and  $\text{ZnAl}_2\text{O}_4$  inclusions significantly reduces the charge carrier mobility (Fig. 5d) due to the decrease in the ceramic density (Fig. 5a). The increase in the doping level is accompanied by a decrease in the doping efficiency (Fig. 5c) and charge carrier mobility (Fig. 5d), which leads to an increase in the resistivity at any used dopant (Fig. 5b).

For sintering more conductive ceramics, the initial powder can be compacted under high pressure. The increase in compacting pressure from 5 to 150 atm increases the density of ZnO:Al:Cl ceramics (AOn dopant, 2 at.% Al) to  $4.3 \text{ g/cm}^3$  and reduces resistivity to  $1.1 \times 10^{-2} \Omega \text{ cm}$  (Fig. 5a, inset). Additional annealing of this ceramics in Zn vapors does not significantly affect the stoichiometric deviation and concentration of intrinsic donor defects; resistivity after this annealing slightly decreases from  $1.1 \times 10^{-2} \Omega \text{ cm}$  to  $9.5 \times 10^{-3} \Omega \text{ cm}$  (Fig. 5b, inset). Thus, ZnO:Al:Cl CVT ceramics sintered with HCl is saturated by Zn. This effect is important for electrical properties of ZnO:Al thin films (Sect. 4.2). At the same time, annealing in air suppresses Zn excess in ceramics, lowers concentration of  $V_{\text{O}}$ , and increases density of zinc vacancies acting as compensating acceptor defects. As a consequence, the resistivity increases to  $126 \Omega \cdot \text{cm}$ . This effect of annealing in air was previously observed for ceramics and ZnO thin films [9, 29]. Annealing in vacuum at  $400 \text{ }^\circ\text{C}$  for 30 min leads to a twofold decrease in the electrical resistance of the ceramic samples (Fig. 5c, inset). This is attributed to cleaning surface from salts (chlorides), adsorbed gases and water. Thus, the investigated ceramics can be used as stable highly conductive targets for a high-power magnetron sputtering in vacuum.

The proposed sintering method has several important advantages. (i) The decrease in the sintering temperature to  $1070 \text{ }^\circ\text{C}$  owing to a rapid growth

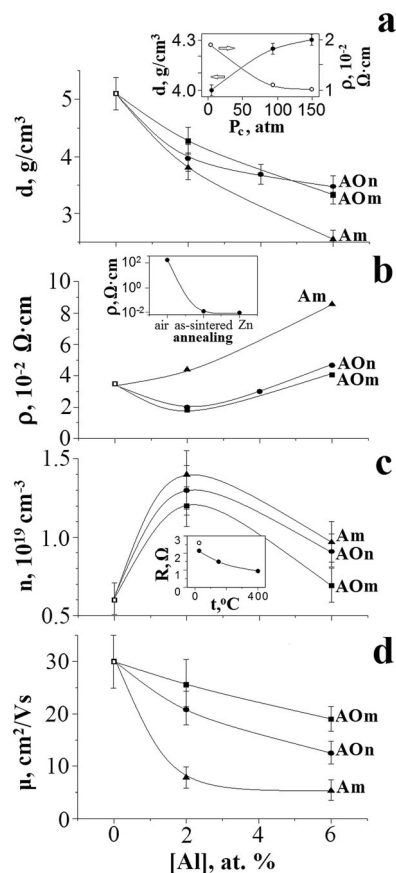
**Fig. 3** Top-view SEM images registered with BSE detector of ZnO:Al:Cl ceramics doped with **a** AOm, **b** AOn, and **c** Am (2 at.% Al). The concentration of Al in impurity precipitations is indicated



**Fig. 4** Normalized XRD spectra of ZnO ceramics doped with (a) AOm, (b) AOn, and (c) Am (2 at.% Al). Inset illustrates the spectra of ceramics doped with AOn; Al concentration is indicated in at. %

of ZnO microcrystals due to CVT based on HCl [9]. (ii) The absence of deviation in the diameter of the ceramics; about  $99 \pm 1\%$  of the initial diameter can be achieved. (iii) The low cost of Al micropowder used as a dopant. (iv) The presence of Zn excess in ceramics, leading to enhanced electrical properties of ZnO:Al thin films (Sect. 4.2).

The interaction of  $\text{In}_2\text{O}_3$  and  $\text{ZnCl}_2$  vapors is too intensive. The condensate of indium chlorides was observed on walls of the sintering chamber after annealing  $\text{ZnO} + \text{In}_2\text{O}_3$  powder in the presence of HCl. Obviously, this interaction is more intense than the thermodynamic estimations (Sect. 2) due to the presence of unconsidered complex chlorides, such as  $\text{In}_4\text{Cl}_7$ ,  $\text{In}_2\text{Cl}_3$ ,  $\text{In}_3\text{Cl}_4$  or substances formed by interaction of indium chlorides and  $\text{H}_2\text{O}$ . Therefore, there is an essential loss of  $\text{In}_2\text{O}_3$  dopant, which reaches 79%. The sintering ZnO powder is carried out with the participation of  $\text{ZnCl}_2$  vapors (Eq. 1). The dense medium of indium chlorides suppresses  $\text{ZnCl}_2$  vapor pressure; consequently, the resulting ZnO:In:Cl material (2 at.% In) is characterized by a relatively low density and hardness of about  $3.7 \text{ g/cm}^3$  and 0.5



**Fig. 5** The effect of the dopant concentration on the **a** density, **b** resistivity, **c** charge carrier concentration, and **d** electron mobility of ceramics. Insets: **a** density and resistivity of ceramics as a function of compacting pressure, **b** effect of annealing on the resistivity of ceramics, **c** influence of the annealing temperature in a vacuum upon electrical resistance of ceramics (AOn dopant, 2 at.% Al, open symbol corresponds to as-sintered ceramics)

GPa, respectively, as well as by a high resistivity of  $5.1 \times 10^{-2} \Omega \text{ cm}$ . The XRD spectrum contains preponderantly peaks related to ZnO; several weak peaks attributed to  $\text{Zn}_7\text{In}_2\text{O}_{10}$  are also observed at a

maximum doping level of 6 at.% (Fig. 6a). Essential dopant inclusions are not observed (Fig. 6b).

Comparative analysis of ZnO CVT ceramics doped by Al, Ga and In is presented in Table 1 containing also concentration of loaded dopant ( $[Me]_{load}$ ) and relative amount of metal impurity present in the ceramics after the sintering process ( $[Me]/[Me]_{load}$ ). These results corroborate the thermodynamic estimations discussed in Sect. 2. (i) The dissolution rate of  $Al_2O_3$  by the CVT based on HCl is essentially lower compared to Ga or In impurities. Undissolved dopant inclusions decrease density, hardness and conductivity of ZnO ceramics. High compacting pressure is necessary to obtain more conductive ceramics. Al solubility limit in ZnO ceramics  $\leq 2$  at.%, which corresponds to many previous works [6]. The loss of  $Al_2O_3$  dopant during CVT sintering is negligible. (ii) The solubility limit of Ga is about 5 at.% [10]. The loss of  $Ga_2O_3$  dopant after sintering is 13%. The most conductive ZnO:Ga:Cl ceramics with loading 3 mol %  $Ga_2O_3$  has the following parameters:  $\rho = 1.5 \times 10^{-3} \Omega \cdot cm$ ,  $n = 5.4 \times 10^{19} cm^{-3}$ ,  $\mu = 80 cm^2/Vs$  and density of  $5.3 g/cm^3$  [10]. The intensity of  $Ga_2O_3 + ZnCl_2$  reaction and dissolution rate of  $Ga_2O_3$  by the CVT based on HCl is relatively high;  $Ga_2O_3$  micropowders with the particles size of 10–50  $\mu m$  can be effectively used as a dopant [10]. (iii) The intensity of  $In_2O_3 + ZnCl_2$  interaction is too high. For a decrease in the loss of  $In_2O_3$  dopant ( $\sim 79\%$ ), different TAs should be used.

Thus, HCl-based CVT can be proposed as an alternative technique for obtaining stable and highly conductive ZnO:Al ceramic targets with Zn excess

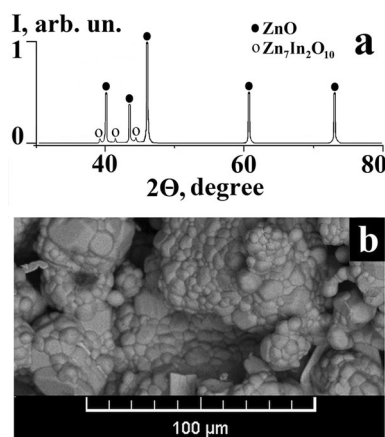
using metallic Al or  $Al_2O_3$  nanopowder as dopants. Due to the solubility limit of Al in ZnO, the too weak interaction between  $Al_2O_3$  and HCl, and the relatively low dissolution rate of  $Al_2O_3$ , the recommended doping level is about 2 at.%. A further increase in the doping level significantly reduces the density of the resulting material.

## 4.2 ZnO:Al:Cl thin films

XRD measurements of ZnO:Al:Cl thin films reveal an intensive (002) reflection peak (Fig. 7a), confirming the high structural quality of the obtained films. The average transparency of the films in the visible spectral range is 81%, being close to the value of films obtained from unintentionally doped ZnO:Cl ceramics (Fig. 7b). The optical band gap energy of ZnO:Cl films is 3.32 eV, which is close to the band gap energy of undoped ZnO [1, 30, 31]. For the most conductive ZnO:Al:Cl samples (deposited at 150 °C–200 °C, 2 at.% Al, AOn dopants), the optical band gap energy reaches the value of 3.63 eV (Fig. 7b). The observed optical band gap shift caused by the well-known Burstein–Moss effect [32] is equal to 310 meV. This indicates the high free electron concentration in Al-doped ZnO films.

The influence of various technological factors on the electrical properties of ZnO:Al:Cl thin films is summarized in Fig. 8. ZnO films deposited using ZnO:Al:Cl ceramic targets doped with AOm have a relatively high value of resistivity ( $1.3 \times 10^{-3} \Omega cm$ ) and low value of figure of merit ( $5 k\Omega^{-1}$ ) (Fig. 8a). This effect is attributed to the weak sputtering of  $Al_2O_3$  or  $ZnAl_2O_4$  dielectric inclusions (DC magnetron sputtering) present in targets (Fig. 3a). The use of AOn dopant for ceramics is more promising; resistivity of corresponding thin films decreases to  $5.1 \times 10^{-4} \Omega cm$ , and figure of merit increases to  $16 k\Omega^{-1}$ . ZnO thin films with similar electrical properties can be obtained using ceramic targets doped with a pure Al micropowder (Fig. 8a).

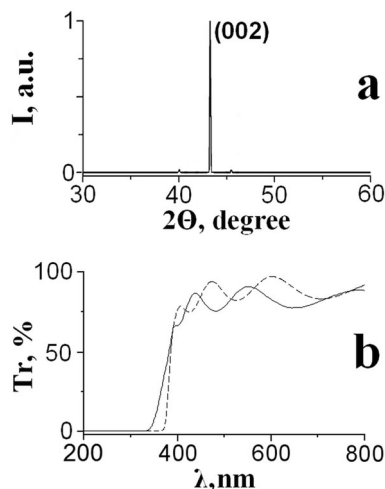
ZnO films deposited using an unintentionally doped ZnO:Cl ceramics have a low value of resistivity and free carrier concentration ( $4.0 \times 10^{-3} \Omega cm$  and  $4 \times 10^{19} cm^{-3}$ , respectively). This is caused by the low concentration of residual donors and Cl impurity in the used targets ( $\sim 4 \times 10^{19} cm^{-3}$  [28]). Adding 2 at.% Al (AOn dopant) increases value of n



**Fig. 6** a XRD spectrum and b top-view SEM image registered with BSE detector of ZnO:In:Cl ceramic surface (6 at.% In)

**Table 1** The main parameters of the most conductive ZnO CVT ceramics doped with Al, Ga and In (compacting pressure 5 atm)

Ceramics	[Me] <sub>load</sub> , at.%	<i>d</i> , g/cm <sup>3</sup>	H, GPa	$\rho$ , 10 <sup>-2</sup> Ω cm	[Me]/[Me] <sub>load</sub>
ZnO:Cl	–	5.1	2.0	3.5	–
ZnO:Al:Cl	2 (AOn dopant)	4.0	1.1	1.8	0.99
ZnO:Ga:Cl	6	5.3	2.5	0.15	0.87
ZnO:In:Cl	2	3.7	≤0.5	5.1	0.21

**Fig. 7** **a** XRD spectrum and **b** transmittance spectrum of ZnO:Al:Cl thin film (ceramic target doped with AOn, 2 at.% Al; dashed line corresponds to the undoped film)

to  $5 \times 10^{20} \text{ cm}^{-3}$ , causing the decrease in resistivity to  $5.1 \times 10^{-4} \text{ Ω cm}$ . A further increase in Al concentration in targets has no essential effect on the conductive properties of ZnO films (Fig. 8b) being attributed to the limited solubility of Al.

The influence of the deposition temperature is shown in Fig. 8c. ZnO:Al:Cl thin films deposited at 120 °C have a relatively low value of  $n$  ( $3 \times 10^{20} \text{ cm}^{-3}$ ) and high resistivity of  $7.3 \times 10^{-4} \text{ Ω cm}$ . The increase in the deposition temperature to 150 °C–200 °C contributes to a better incorporation of Al impurity, an increase in concentration and mobility of charge carriers ( $5 \times 10^{20} \text{ cm}^{-3}$  and  $26 \text{ cm}^2/\text{Vs}$ , respectively), leading to a decrease in resistivity to  $4.5 \times 10^{-4} \text{ Ω cm}$ . A further increase in the deposition temperature up to 250 °C slightly decreases concentration and mobility of free electrons, increasing value of  $\rho$  to  $6.1 \times 10^{-4} \text{ Ω cm}$ . Similar temperature dependences were observed by authors of Ref. [33], attributed to the formation of Al precipitations in thin films deposited at temperatures  $\geq 200 \text{ °C}$ .

The effect of ceramic targets, obtained in various gaseous media, is analyzed in Fig. 8d. The use of classical ZnO:Al ceramic targets (2 at.% Al, AOn

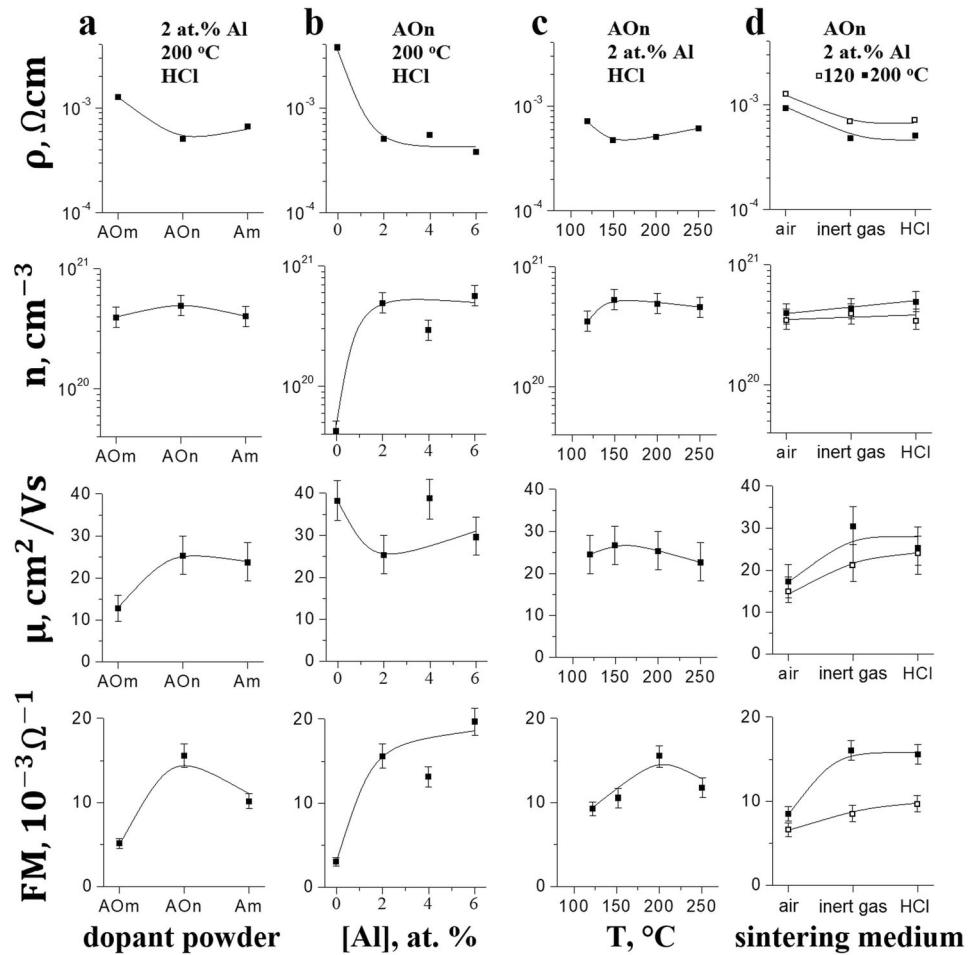
dopant) sintered in air gives the possibility to deposit thin films with a relatively high  $\rho$  value of  $9.2 \times 10^{-4} \text{ Ω cm}$ , and low FM value of  $8 \text{ kΩ}^{-1}$  (200 °C deposition). Such ceramic targets should have a negligibly small Zn excess (Sects. 1, 4.1). ZnO:Al ceramic targets sintered in inert gas atmosphere should have a higher concentration of intrinsic donor defects related to Zn excess. Thin films deposited using such ceramics are characterized by higher conductivity, concentration and mobility of charge carriers:  $\rho = 4.9 \times 10^{-4} \text{ Ω cm}$ , FM =  $18 \text{ kΩ}^{-1}$  (Fig. 8d). ZnO:Al:Cl CVT ceramics sintered using HCl have the same Zn excess and residual Cl impurity. ZnO films obtained using this type of ceramics and co-doped with Cl have similar electrical properties (Fig. 8d). Thus, the interaction of Cl and Al impurities is relatively low at the deposition process and has no significant effect upon the properties of ZnO thin films. This result differs from Ga + Cl co-doping leading to a decrease in the resistivity of films by 2 times [21]. The resistivity of ZnO:In:Cl thin films deposited using CVT ceramic targets is as high as  $6.4 \times 10^{-3} \text{ Ω cm}$ , which is attributed to the high loss of  $\text{In}_2\text{O}_3$  dopant in the sintering process (Sect. 4.1).

## 5 Conclusion

The chemical vapor transport based on HCl can be proposed as an alternative technological approach for sintering ZnO:Al:Cl ceramics using metallic Al or  $\text{Al}_2\text{O}_3$  nanopowder as dopants. The advantages of the proposed method consists in: (i) the decrease in the sintering temperature to 1070 °C; (ii) the absence of deviation in the diameter of ceramics; (iii) controllable Zn excess in ceramics; (iv) the low cost of Al micropowder, which can be used as a dopant. The conductive properties of ZnO:Al:Cl ceramics are sensitive to powder compacting pressure and to stoichiometric deviation. The density of  $4.3 \text{ g/cm}^3$  and resistivity of  $9.5 \times 10^{-3} \text{ Ω cm}$  are reached using 150 atm compacting pressure and Zn excess in ceramics.



**Fig. 8** Resistivity, charge carrier concentration and mobility, as well as figure of merit for ZnO:Al:Cl thin films as a function of **a** dopant powder, **b** concentration of Al, **c** deposition temperature, and gaseous medium of sintering ceramic target in **(d)**



The theoretical and experimental comparative analysis of sintering ZnO:Me:Cl CVT ceramics (Me = Al, Ga, In) has been carried out. The interaction between Al<sub>2</sub>O<sub>3</sub> and ZnCl<sub>2</sub> (HCl) and dissolution rate of dopant are relatively weak, the solubility of Al in ZnO ceramics is limited, and the recommended doping level is about 2 at.%. A further increase in the dopant concentration significantly reduces the density and conductivity of the resulting material. The loss of Al<sub>2</sub>O<sub>3</sub> dopant during CVT sintering is negligibly small. The intensity of interaction between In<sub>2</sub>O<sub>3</sub> and ZnCl<sub>2</sub> is too high; the loss of In<sub>2</sub>O<sub>3</sub> dopant is about 79%, and resistivity of ZnO:In:Cl CVT ceramics is as high as  $5.1 \times 10^{-2} \Omega \text{ cm}$ . It was established that Ga<sub>2</sub>O<sub>3</sub> is the most suitable dopant for CVT sintering ZnO ceramics. The moderate interaction of Ga<sub>2</sub>O<sub>3</sub> with ZnCl<sub>2</sub> (HCl), the high solubility limit and dissolution rate of Ga<sub>2</sub>O<sub>3</sub> in ZnO contribute to obtaining of ceramics with a density of 5.3 g/cm<sup>3</sup> and resistivity as low as  $1.5 \times 10^{-3} \Omega \text{ cm}$ .

ZnO:Al:Cl CVT ceramics can be used as magnetron targets to deposit ZnO thin films with a resistivity of at least  $4.5 \times 10^{-4} \Omega \text{ cm}$  and a value of figure of merit of  $16 \text{ k}\Omega^{-1}$  (650 nm thickness, 150 °C–200 °C deposition). Zn excess in ZnO:Al:Cl ceramic targets contributes to a decrease in the resistivity of thin films by 2 times. The interaction of Cl and Al in the deposition process is too weak; the presence of the residual Cl impurity in targets has no significant effect on the conductive properties of the deposited films.

### Author contributions

Contribution of GVC is thermodynamic calculations, ceramic sintering, thin film deposition, theoretical and experimental analysis, and manuscript preparation; DR, NC and OS investigated optical/electrical properties, XRD, and ceramic hardness, respectively; contribution of EVM is SEM and EDX measurements.

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## Data availability

This manuscript has no associated data.

## Declarations

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

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