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Low-temperature sintering of highly conductive ZnO:Ga:Cl ceramics by means of chemical vapor transport

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ABSTRACT

A new technology for sintering a ZnO + Ga_2O_3 powder via chemical vapor transport based on HCl has been developed. The proposed sintering method has the following advantages: a low sintering temperature of 1000–1100 °C, there is no need to use of expensive dopant nanopowders, the possibility of multiple re-sintering, and the absence of changes in the diameter of the ceramics after sintering. A ZnO:Ga:Cl ceramics with a density of 5.31 g/cm^3, a hardness of 2.0 GPa, and a resistivity of 1.46×10^{-3} Ω·cm has been synthesized. The solubility limit of the Ga_2O_3 dopant has been estimated at about 3 mol %. At a higher doping level, the content of the $ZnGa_2O_4$ spinel phase becomes significant. In addition, ZnO:Ga:Cl thin films with a resistivity of 2.77×10^{-4} Ω·cm can be grown by DC magnetron sputtering of the synthesized ceramics.

1. Introduction

Over the last two decades, ZnO thin films have shown broad prospects for application, in particular, in light-emitting and photoconductive devices, piezoelectric transducers, and gas sensors [1]. One of the simplest methods to obtain highly conductive thin films is DC magnetron sputtering; however, the efficiency of this method is based on the presence of uniformly doped conductive ceramic targets [1]. The most commonly used sintering method consists in compacting a powder of ZnO and a dopant with subsequent annealing in air or an inert gas atmosphere. The method has the following disadvantages [2–4]: (i) the necessity to use a high-pressure technology (≥ 100 MPa); (ii) extremely high sintering temperatures of about 1300–1500 °C, which are required to obtain materials with a fairly high hardness, density, uniformity, and conductivity; (iii) the necessity to use expensive dopant nanopowders; (iv) a change in the diameter of the ceramics after sintering; and (v) difficulties in re-sintering of the sputtered or partially destroyed ceramics.

Dielectric dopant inclusions in ceramic targets complicate the deposition of ZnO thin films with a uniform doping level. Extremely high temperatures and the use of dopant nanopowders are required to increase the rate of physical and chemical reactions accompanying the dissolution of the dopant in the ceramics. The chemical vapor transport (CVT) technique can be proposed as an alternative approach to sintering ceramics. A high pressure of doping gaseous species involved in CVT reactions can contribute to the formation of ceramics uniformly doped in the gas phase even at low sintering temperatures. Several transport agent (TA) mixtures based on HCl were proposed for an unseeded growth of high-quality ZnO single crystals [5–8]. Subsequently, these TAs were proposed for sintering ZnO:Cl ceramics. An unintentionally doped material with a high density and hardness, a moderate conductivity, and a controllable stoichiometric deviation was synthesized at a temperature as low as 1070 °C [9]. Unfortunately, the Cl donor concentration in this material (10^{19} cm^{-3}) is not sufficiently high, and the development of a technology for producing highly doped ZnO ceramics via CVT is necessary to obtain conductive ZnO thin films. The doping efficiency of these CVT ceramics with oxides of various metals was calculated in Ref. [9,10]; a promising doping with some metal oxides, in particular, Ga_2O_3, was predicted.

The most typical donors for ZnO are Al, Ga, and In; however, Ga is less reactive and more resistant to oxidation than Al. The Ga–O covalent bond length (1.92 Å) is close to that of Zn–O (1.97 Å); this factor provides a decrease in the deformation of the ZnO lattice even at a high doping level [11]. The data on the Ga solubility limit in ZnO are controversial. The authors of [12–14] estimated this value at 0.5–2.5 at %. At the same time, the solubility of 4.5 at % was achieved in ZnO:Ga films [15]. A lot of studies were dedicated to obtaining highly conductive ZnO:Ga thin films. For example, films with a resistivity (ρ) of

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3.8×10^{-4} Ω·cm were grown at 250 °C by magnetron sputtering of ZnO:Ga ceramic targets by authors of [15]. Unfortunately, at a deposition temperature of 100 °C, these films generally exhibit a higher resistivity of about 10^{-3} Ω·cm [15], while low-temperature deposition (≤ 100 °C) is more preferable for manufacturing solar cells and some other devices. The ZnO:Ga:Zn thin films obtained via sputtering of ZnO:Ga:C composite targets had a ρ value of 2.5×10^{-4} Ω·cm (deposition at 300 °C); however, at lower growth temperatures, these films showed a significant Zn excess and a low transparency in the visible spectral range [16]. One of the lowest resistivities achieved and reported for ZnO:Ga films deposited at room temperature by magnetron sputtering is 2.8×10^{-4} Ω·cm [17]. These films are characterized by a high thickness of about 1100 nm and, as a consequence, a relatively low transparency of ≤ 80 %.

This study addresses a novel approach to sintering highly conductive cation-doped ZnO ceramics using CVT reactions based on HCl. A low sintering temperature (< 1100 °C); a high hardness, density, and conductivity of the ceramics; the absence of changes in the diameter of the sintered material; the possibility of multiple re-sintering; and the use of a dopant powder with a relatively large particle size are the purposes of this study.

2. Preliminary thermodynamic notes

The saturated vapor pressure of many metal oxides is extremely low. This factor is responsible for the weak dissolution rate of the dopant, if ZnO ceramics is sintered at relatively low temperatures (~ 1000 °C) in air or an inert gas atmosphere. For example, the saturated vapor pressure of Ga_2O_3 (Ga_2O + O_2) at 1000 °C is as low as 10^{-10} atm [18]. A similar weak dissolution rate of the dopant can be expected, if ceramics is sintered by CVT reactions using classical TAs, such as H_2, C, and CO, which weakly interact with ZnO [5]. The interaction of ZnO and HCl is more intensive; HCl is almost completely transformed into $ZnCl_2$ and H_2O [5]. Zinc chloride vapors can act as a TA for various oxides and, thereby, provide the dissolution of various dopants in ZnO [9,10]. The interaction between a 3-valent metal oxide (Me_2O_3) and $ZnCl_2$ can be described as follows:

$$Me_2O_3 + 3ZnCl_2(gas) \leftrightarrow 2MeCl_3(gas) + 3ZnO \quad (1)$$

The equation for pressures of the gaseous species participated in reaction (1) is as follows [10]:

$$P^2_{MeCl_3} = K^p P^3_{ZnCl_2}, \quad (2)$$

where K_p is the equilibrium constant of this reaction. A higher pressure of doping chlorides ($MeCl_3$) should cause a more intensive doping of ZnO during sintering. Fig. 1 shows the calculated $MeCl_3$ vapor pressure over Me_2O_3 + ZnO in the presence of $ZnCl_2$, if the initial pressure of $ZnCl_2$ ($ZnCl_2{}^{\circ}$) is 1 atm and Me = Al, Ga, and In. The interaction of $ZnCl_2$ and Al_2O_3 is relatively low. It is obvious that the $AlCl_3$ pressure is too low for an effective doping of ZnO. A chemically more intensive TA should be used instead of HCl ($ZnCl_2$) to obtain uniformly doped ZnO:Al ceramics. The interaction of $ZnCl_2$ and In_2O_3 seems to be too intensive, and the $InCl_3$ pressure is too high (Fig. 1). It is reasonable to expect a certain loss in the amount of In_2O_3, because a portion of the In dopant should remain in the vapor phase. At the same time, the $GaCl_3$ equilibrium vapor pressure seems to be optimal at 10^{-3} atm for a wide temperature range, and an effective doping with Ga_2O_3 should be expected even at temperatures as low as 1000–1100 °C.

ZnO–Ga_2O_3–$ZnCl_2$ CVT systems should be extremely sensitive to the presence of additional Zn vapors. A Zn + $ZnCl_2$ mixture should interact with Ga_2O_3 more effectively, generating additional $GaCl_2$ and GaCl vapors [10]. At the same time, an increase in the pressure of $GaCl_n$ substances can affect the dissolution rate and the loss of the Ga_2O_3 dopant.

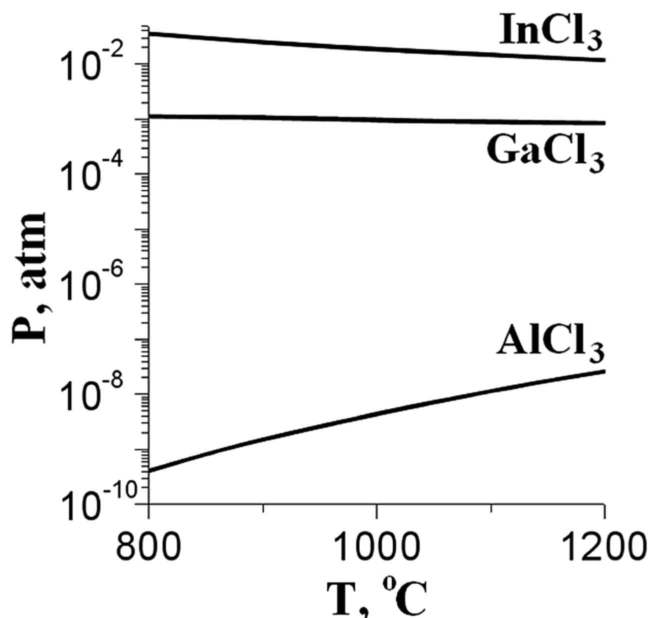

Fig. 1. Temperature dependence of $MeCl_3$ vapors in the ZnO–Me_2O_3–$ZnCl_2$ CVT systems (Me = Al, Ga, In) at $ZnCl_2{}^{\circ}$ = 1 atm.

3. Experiment

Ceramics was sintered by means of CVT in sealed quartz chambers at 1070 °C for 48 h. A ZnO + Ga_2O_3 mixed powder was loaded on the flat bottom of chambers; the typically used strong compression of the powder was not applied. Before loading TAs, the sintering chamber and the material were purified by annealing in a dynamic vacuum. The technological details of sintering were described earlier in [9]. A ZnO powder (99.98 %) with a particle size of 30–100 μm and a Ga_2O_3 powder (99.99 %) with a particle size of 10–50 μm were used as the material source. The Ga_2O_3 dopant concentration was varied in a range of 0–10 mol %. Hydrogen chloride was used as a typical TA at a loading pressure of 2 atm at the sintering temperature. Hydrogen chloride generates only $ZnCl_2$ + H_2O vapors [5]; it was used to obtain ceramics without any stoichiometric deviation. Several comparative experiments with HCl + H_2 and HCl + H_2 + C TAs generating $ZnCl_2$ + Zn vapor media [9,10] were used to obtain ceramics with a Zn excess. The typical dimension of the sintered ceramics was 25 mm in diameter and 1 mm in thickness.

Before studying electrical properties, all the ceramic samples were purified by annealing in a dynamic vacuum at 300 °C for 30 min. The resistivity, charge carrier concentration (n), and Hall mobility (μ) of the ceramics and thin films were calculated from the Hall effect measurements by the van der Pauw method in a magnetic field of 1 T using In droplets fused to the sample surface as the electrical contacts. 2Θ X-ray diffraction (XRD) spectra, recorded using FeK_{α} radiation (1.936 Å), were used to analyze the crystallinity and composition of the samples. A Zeiss Sigma scanning electron microscope (SEM) (with a secondary electron detector and a back scattered electron detector) and a TESCAN Vega TS 5130 MM SEM equipped with an Oxford Instruments INCA energy dispersive X-ray analysis (EDX) system were used to study the morphology and for chemical composition microanalysis. For analysis of grain size distribution, the as-sintered ceramics was polished with a 1 μm diamond paste and then etched in a 0.5 % HCl aqueous solution for 30–90 s to delineate grain boundaries. The mean grain sizes were measured using the image analysis software. To evaluate the thermal stability of conductive properties, ZnO ceramics was annealed in a temperature range of 20–600 °C in a low dynamic vacuum of 10^{-4} atm 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 (20–25 °C).

ZnO:Ga:Cl thin films were grown on glass substrates by DC magnetron sputtering. The synthesized ZnO:Ga:Cl ceramic sample with 3 mol % Ga_2O_3 with a diameter of 25 mm and a thickness of 1 mm was used as the target. To conduct a comparative study, several unintentionally doped ZnO:Cl thin films were grown from ZnO:Cl ceramics. Argon with a purity of 99.998 % and a pressure of $4{\cdot}10^{-6}$ 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 100–200 °C. The typical thickness of the ZnO:Ga:Cl films was 700–800 nm. Post-growth annealing was not used in any of the cases.

4. Experimental results and discussion

4.1. ZnO:Ga:Cl ceramics: general characterization and advantages

Significant changes in the properties of the sintered ceramics were observed upon the addition of 1 mol % Ga_2O_3 to a ZnO powder. The resulting material was black in color, which indicates a high level of doping with Ga, while the unintentionally doped CVT ZnO:Cl ceramics synthesized under the same conditions was characterized by light grey color. The presence of Ga impurity was confirmed by EDX spectroscopy. The Cl impurity concentration was about 10^{19} cm^{-3} [19]. Undissolved Ga_2O_3 particles were not observed anywhere. Analysis of the XRD spectra reveals the same peaks that are observed in the undoped ZnO:Cl ceramics (Figs. 2a, 2b). All the peaks are attributed to hexagonal ZnO; there are no significant reflection lines attributed to Zn, $ZnCl_2$, undissolved Ga_2O_3, or $ZnGa_2O_4$. Finally, the resistivity decreases 12-fold to $(3 \pm 0.2) \times 10^{-3}$ Ω·cm; this fact indicates a high concentration of shallow donors [20] (Section 4.3). Thus, these characteristics confirm the complete dissolution of Ga_2O_3 in ZnO ceramics at a temperature of 1070 °C.

The ZnO:Ga:Cl ceramics has a high density of 5.31 ± 0.19 g/cm^3, which corresponds to 94.5 ± 3.4 % of the theoretical value of 5.62 g/cm^3 [21]. The hardness is 2.0 ± 0.2 GPa, which is close to the hardness of ZnO single crystals [22]. Thus, this material can be used for magnetron sputtering (Section 4.4). The thickness of the sintered materials decreases by about 2.5 times during annealing. At the same time, a diameter of 99 ± 1% of the initial diameter can be achieved by this sintering method due to the tendency of CVT growing on a relatively cold bottom of the growth chamber [9]. The thickness of the ceramics can be varied at least in a range of 0.75–4 mm. The typically used strong compressing of the powder is not obligatory for the proposed sintering method [9]. This factor provides conditions for multiple re-sintering. An essentially sputtered ceramics with a minimal thickness of about 0.1 mm and ceramics with a destroyed periphery can be resintered with an additional material to achieve the typical size. This re-sintered ceramics was effectively used as a magnetron target.

The proposed sintering method has three important advantages in addition to the possibility of re-sintering and the absence of deviation in the diameter of the ceramics. (i) The sintering temperature can be decreased to 1000–1100 °C owing to a rapid growth of ZnO microcrystals by means of CVT reactions. The ceramics with a similar high density, hardness, and conductivity can be synthesized by the classical methods at temperatures as high as 1300–1500 °C [3,4]. The temperature used in this study is optimal: at temperatures of < 1000 °C, the density and hardness of the ceramics are not sufficiently high, while at temperatures of > 1100 °C, the softening and gradual deformation of the quartz sintering chamber should occur [9]. (ii) There is no necessity to use expensive dopant nanopowders. Doping is conducted by a rapid diffusion of $GaCl_3$ vapors having a fairly high pressure of about 10^{-3} atm (Fig. 1). The recommended dopant particle size is < 100 μm. In the case of Ga_2O_3 particles with a larger diameter and for ZnO particles with a

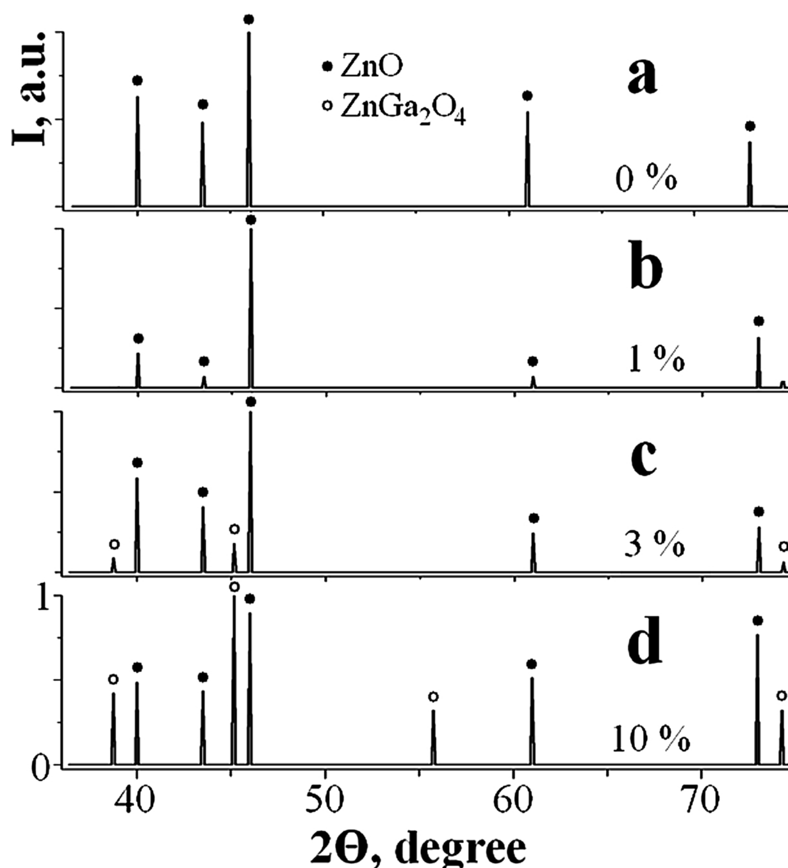

Fig. 2. Normalized XRD spectra of ZnO ceramics with (a) 0, (b) 1, (c) 3, and (d) 10 mol % Ga_2O_3.

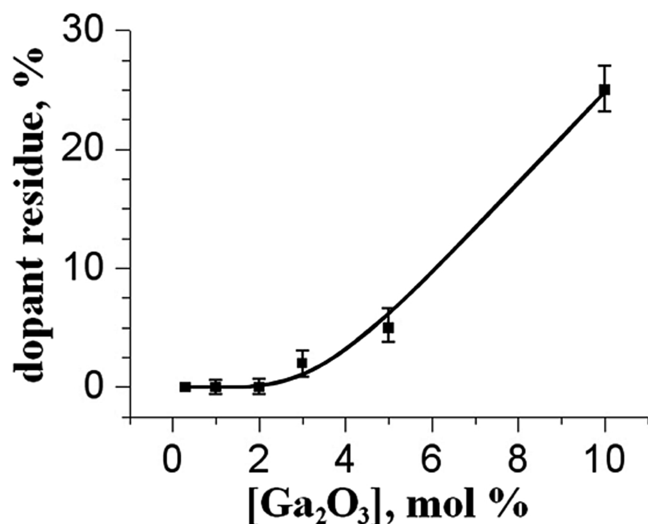

Fig. 3. Undissolved Ga_2O_3 residue as a function of the amount of the loaded dopant.

size of ≥200 μm, the studied material showed a lower uniformity. The $GaCl_3$ pressure and the dopant dissolution rate can be increased at a higher pressure of HCl^o; however, the use of a denser HCl medium causes a decrease in the sintering rate [9]. (iii) The Cl impurity concentration in the synthesized ceramics is about 10^{19} cm^{-3} [19]; that is, this impurity is not the basic impurity. At the same time, the presence of Cl significantly improves the incorporation of the basic impurity (Ga, Al, In) into the ZnO lattice at low temperatures and increases the conductivity of ZnO thin films (Section 4.4).

4.2. ZnO:Ga:Cl ceramics: effect of doping level on the structural properties and solubility limit of the dopant

The ZnO:Ga:Cl ceramics with a loading of 2 mol % Ga_2O_3 exhibited similar properties. In the case of using 3 mol % Ga_2O_3, a thin layer of undissolved dopant particles and the $ZnGa_2O_4$ powder is observed on the upper surface of the ceramics. The weight of this dopant residue is about 1–2% of the weight of the loaded dopant (Fig. 3). X-ray diffraction spectroscopy reveals several peaks attributed to the $ZnGa_2O_4$ spinel phase (Fig. 2c). In the case of 5 mol % Ga_2O_3, the dopant residue increases to 5–7 % (Fig. 3). Finally, the loading of 10 mol % Ga_2O_3 leads to the formation of ceramics with a significant layer of the undissolved dopant and the $ZnGa_2O_4$ powder on the top surface with a weight of about 25 % of the weight of the loaded dopant (Fig. 3). The XRD spectrum reveals several intensive $ZnGa_2O_4$ reflection lines (Fig. 2d). Thus, the experimental results make it possible to estimate the solubility limit of Ga_2O_3 in ZnO at about 3 mol %. This value is higher than some values reported for ceramics sintered by other methods [12,13]. The concentration of 3 mol % is sufficient for obtaining highly conductive ZnO thin films by means of magnetron sputtering (Section 4.4).

The dopant concentration also has an effect on the microstructure of the resulting material. The unintentionally doped ZnO:Cl ceramics consists of grains with an average diameter of 7 μm (Fig. 4a). The material with 1 mol % Ga_2O_3 consists of grains having an average size of 11 μm (Fig. 4b). An increase in the dopant concentration to 10 mol % leads to a further increase in the average grain size to 34 μm (Figs. 4c, 4d, Fig. 5 (inset)). The SEM images of the most highly doped sample (10 mol % Ga_2O_3), which were recorded with a back scattered electron detector, showed the presence of $ZnGa_2O_4$ inclusions (Fig. 4d, white particles) having a mean size of about 5 μm. The ZnO grain size distributions and the values of a mean grain size are shown in Fig. 5.

4.3. ZnO:Ga:Cl ceramics: electrical properties

The electrical properties of the ceramics are summarized in Fig. 6. The unintentionally doped ZnO:Cl ceramics, which was obtained using pure HCl, has the following parameters: $\rho = (35 \pm 2) \times 10^{-3}$ Ω·cm, $n = (0.58 \pm 0.06) \times 10^{19}$ cm^{-3}, and $\mu = 30 \pm 4$ cm^2/Vs (Fig. 6a) [9]. The addition of 1 mol % Ga_2O_3 increases the n and μ values to $(4.1 \pm 0.4) \times 10^{19}$ cm^{-3} and 50 ± 6 cm^2/Vs, respectively, and leads to a decrease in resistivity to $(3 \pm 0.2) \times 10^{-3}$ Ω·cm. The most conductive ceramics ($\rho = (1.46 \pm 0.1) \times 10^{-3}$ Ω·cm, $n = (5.4 \pm 0.5) \times 10^{19}$ cm^{-3}, $\mu = 80 \pm 10$ cm^2/Vs) can be obtained in the case of loading of 3 mol % Ga_2O_3. With a further increase in the doping level, when the solubility limit is reached (Section 4.2), the concentration and mobility of free electrons decrease to $(2.8 \pm 0.3) \times 10^{19}$ cm^{-3} and 12 ± 2 cm^2/Vs, respectively, in the case of 10 mol % Ga_2O_3. In this case, the resistivity increases to $(19 \pm 1) \times 10^{-3}$ Ω·cm (Fig. 6a).

Several ceramics with 1 mol % Ga_2O_3 were synthesized in media with a high pressure of Zn vapors (up to 1 atm) using HCl + H_2 and HCl + H_2 + C as the TAs. It was found that the presence of Zn vapors does not have a significant effect on the electrical properties of the studied material. The concentration of native donor defects, such as interstitial Zn, generated by a Zn excess, is one–two orders of magnitude lower than the Ga concentration [9]. As a consequence, they cannot have a significant effect on the conductivity of the ceramics. At the same time, the complete dissolution of the dopant (1 mol %; Sections 4.1,4.2) is achieved at a $GaCl_3$ pressure of 10^{-3} atm (using simple HCl as the TA); the expected increase in the pressure of volatile Ga species caused by Zn vapors does not have a significant effect (Section 1).

Annealing in a vacuum at 200 °C leads to a decrease in the electrical resistance of the ceramics by 1.5 times; it can be attributed to the cleaning of the surface from adsorbed gases and water (Fig. 6b). An increase in the annealing temperature to 400 °C leads to a further weak decrease in the resistance of the ceramics, whereas after additional annealing at 600 °C the resistance of the ceramics remains almost constant. Thus, the obtained ceramics can be used as highly conductive magnetron sputtering targets in a low vacuum at temperatures of up to 600 °C.

4.4. ZnO:Ga:Cl thin films: prospects for low-temperature growth

The main electrical parameters of ZnO:Cl thin films grown at 200 °C by DC magnetron sputtering of unintentionally doped ZnO:Cl ceramics are as follows: $\rho = (1.2 \pm 0.04) \times 10^{-2}$ Ω·cm, $n = (1.9 \pm 0.19) \times 10^{19}$ cm^{-3}, and $\mu = 26 \pm 3$ cm^2/Vs. The relatively low charge carrier concentration is caused by the low solubility of the Cl donor impurity in ZnO. The use of ZnO:Ga:Cl ceramics with 3 mol % Ga_2O_3 as the target provides the growth of thin films at 200 °C with the following electrical parameters: $\rho = (2.77 \pm 0.1) \times 10^{-4}$ Ω·cm, $n = (1.0 \pm 0.1) \times 10^{21}$ cm^{-3}, and $\mu = 23 \pm 3$ cm^2/Vs. This resistivity value is one of the lowest for ZnO:Ga films grown by magnetron sputtering. It is significant that a decrease in the deposition temperature to 100 °C does not have a significant effect on the free electron concentration (Fig. 7a). Therefore, the resistivity increases slightly to $(3.05 \pm 0.12) \times 10^{-4}$ Ω·cm only due to a decrease in the charge carrier mobility.

X-ray diffraction spectroscopy of the thin films reveals an intensive (002) reflection peak, which confirms the high structural quality of the resulting films (Fig. 7b). The transparency of the films in the visible spectral range is about 80–90 %, which is close to the value for films obtained from unintentionally doped ZnO:Cl ceramics (Fig. 7c). A strong blue shift of the transmittance spectrum edge is observed; it is caused by the filling of the conduction band with electrons (Burstein–Moss shift) (Fig. 7c, inset). The optical band gap energy for the ZnO:Cl sample, which was determined from the optical adsorption spectrum [23], is 3.32 eV, which is close to the band gap energy of undoped ZnO [1,20]. For the most conductive ZnO:Ga:Cl sample obtained at 200 °C, the optical band gap energy is 3.80 eV. The optical

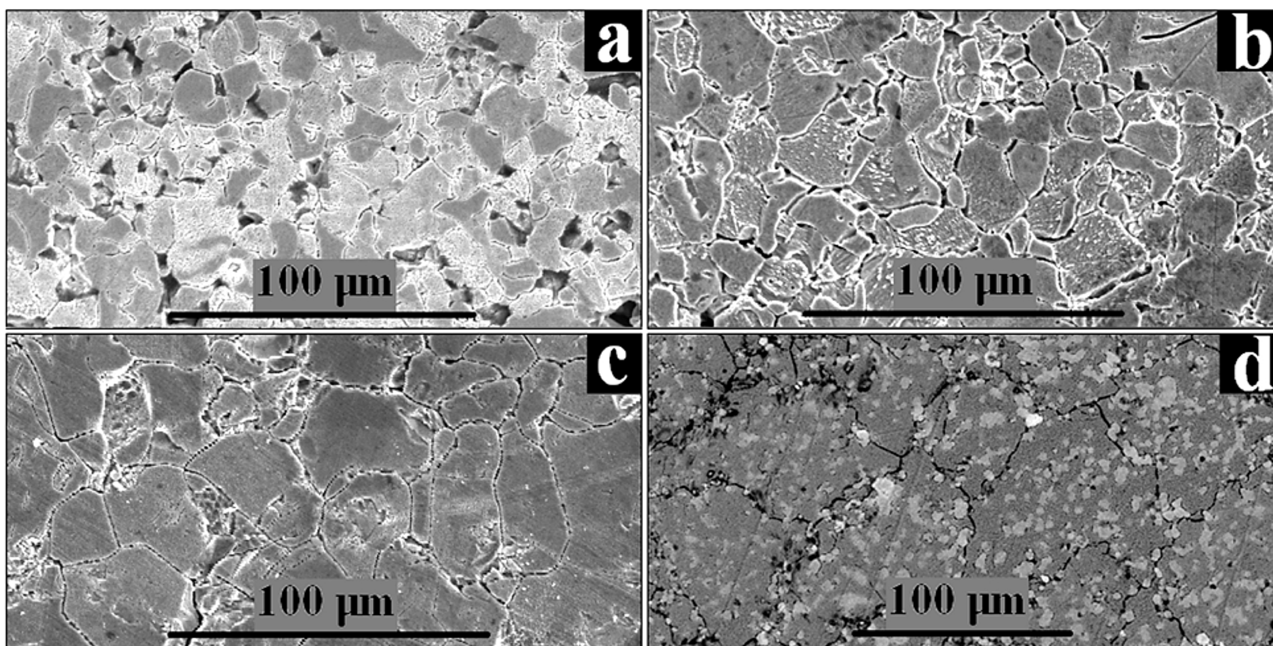

Fig. 4. Scanning electron microscopy image of the surface for ZnO:Ga:Cl ceramics with (a) 0, (b) 1, (c) 3, and (d) 10 mol % Ga_2O_3 measured using (a–c) a secondary electron detector and (d) a back scattered electron detector.

band gap broadening caused by the Burstein–Moss effect reaches 480 meV for the most conductive sample. The free electron concentration corresponding to this optical band gap broadening is $(9 \pm 0.5) \times 10^{20}$ cm^{-3} [24,25], which is consistent with the electrical measurements.

A Ga impurity can form metallic, Ga_2O, GaO, and Ga_2O_3 inclusions or other impurity defects in which Ga atoms do not act as shallow donors. With a decrease in the deposition temperature, the mobility and chemical activity of the atoms decrease and the concentration of these undesirable defects becomes significant, which results in a decrease in the free electron concentration, electron mobility, and transparency of the films [25]. The most interesting fact is the absence of a significant

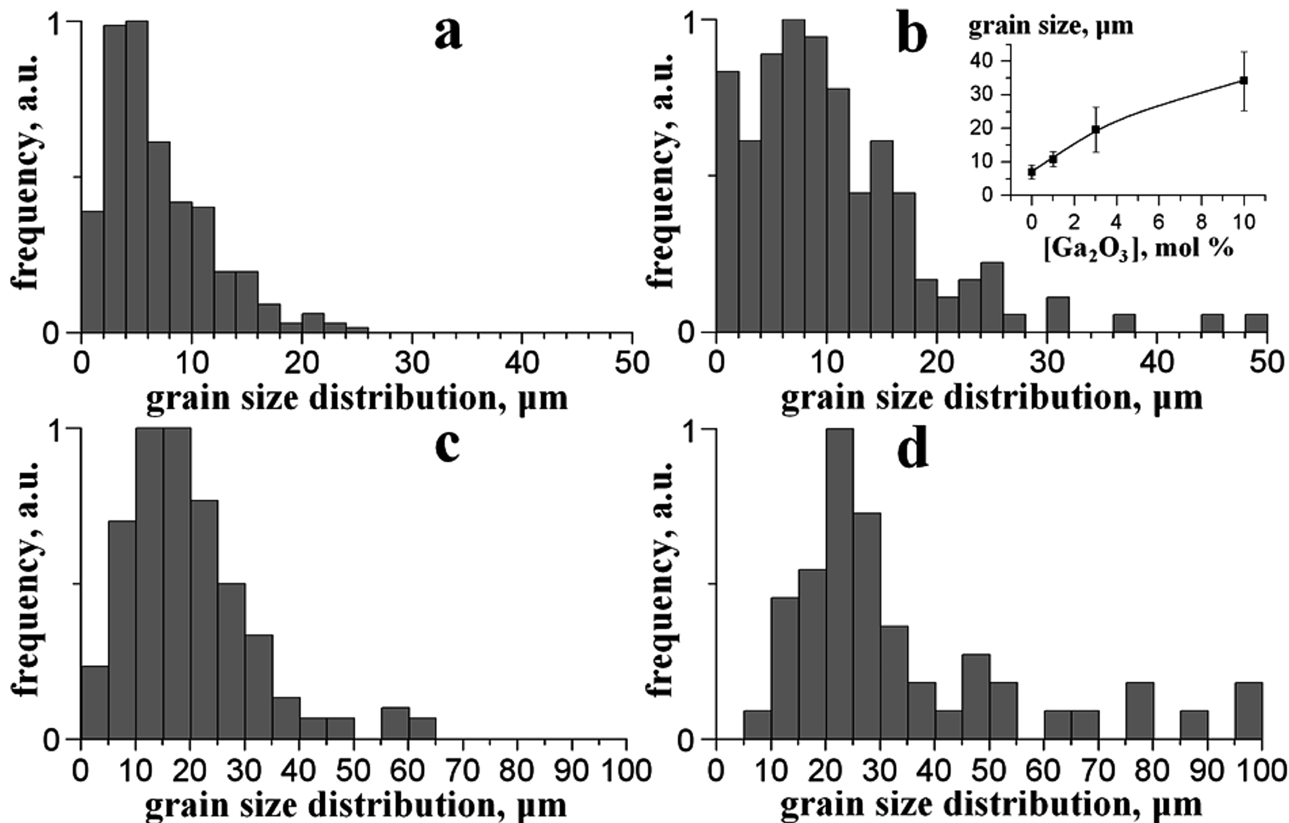

Fig. 5. Grain size distribution of ZnO:Ga:Cl ceramics with (a) 0, (b) 1, (c) 3, and (d) 10 mol % Ga_2O_3. Inset illustrates the average grain size as a function of the doping level.

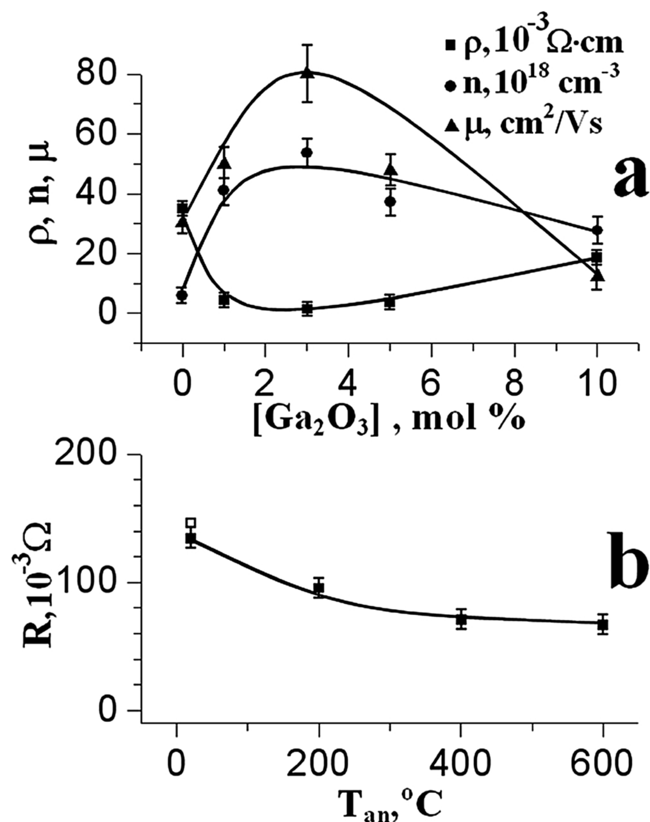

Fig. 6. (a) Effect of the dopant concentration on the resistivity, charge carrier concentration, and electron mobility of ceramics. (b) Effect of the annealing temperature in a vacuum on the electrical resistance of ceramics with 1 mol % Ga_2O_3 (open symbol corresponds to as-sintered ceramics).

temperature dependence of the charge carrier concentration for ZnO:-Ga:Cl thin films. This effect is in conflict with many results obtained earlier: typically, a decrease in the deposition temperature from 200 to 100 °C leads to a decrease in the *n* value by at least 1.5 times [15,16].

This effect can have a simple interpretation. The material sputtered from ZnO:Ga:Cl ceramics can be considered as a flow of a ZnO + Ga_2O_3 + $ZnCl_2$ + $GaCl_3$ mixture. During deposition, some chemical reactions should occur (for example, reaction (1)), and concentration of some species can be determined using the thermodynamic calculation (Eq. (2)). Fig. 8a shows the calculated $P(GaCl_3)/P(ZnCl_2)$ value for various $ZnCl_2$°, where *P* is the equilibrium *thermodynamic* pressure of the indicated vapors. With an increase in $ZnCl_2$°, $P(GaCl_3)/P(ZnCl_2)$ slightly increases; however, it exhibits a similar temperature dependence. The saturated vapor pressure of $GaCl_3$ is extremely high (Fig. 8b), it is many orders of magnitude higher than the pressure of ZnO, Ga, or Ga_2O_3. It means that $GaCl_3$ are very mobile molecules even at low temperatures and they have a large migration length on the ZnO surface. The abovementioned $P(GaCl_3)/P(ZnCl_2)$ value is relatively low: almost all Cl atoms are bound to Zn in $ZnCl_2$ molecules; however, within a short time, some Cl atoms become bonded to Ga in extremely mobile $GaCl_3$ (reaction (1)). Within this short time, $GaCl_3$ molecules pass a fairly long distance and Ga atoms have more probability of incorporating as defects at a minimum free energy (shallow donor defects). Gallium trichloride interacts with the ZnO lattice to generate Ga shallow donors and new $ZnCl_2$ mobile molecules (reverse reaction (1)). Thus, Cl is not the basic impurity; it acts as a catalyst for the better incorporation of the basic impurity. With an increase in the deposition temperature, the $P(GaCl_3)/P(ZnCl_2)$ value decreases, and the amount of Cl bound to Ga also decreases (Fig. 8a). Moreover, with an increase in temperature, some volatile $GaCl_3$ molecules can fly away from the surface; as a consequence, the efficiency of Cl *catalyst* decreases. At the

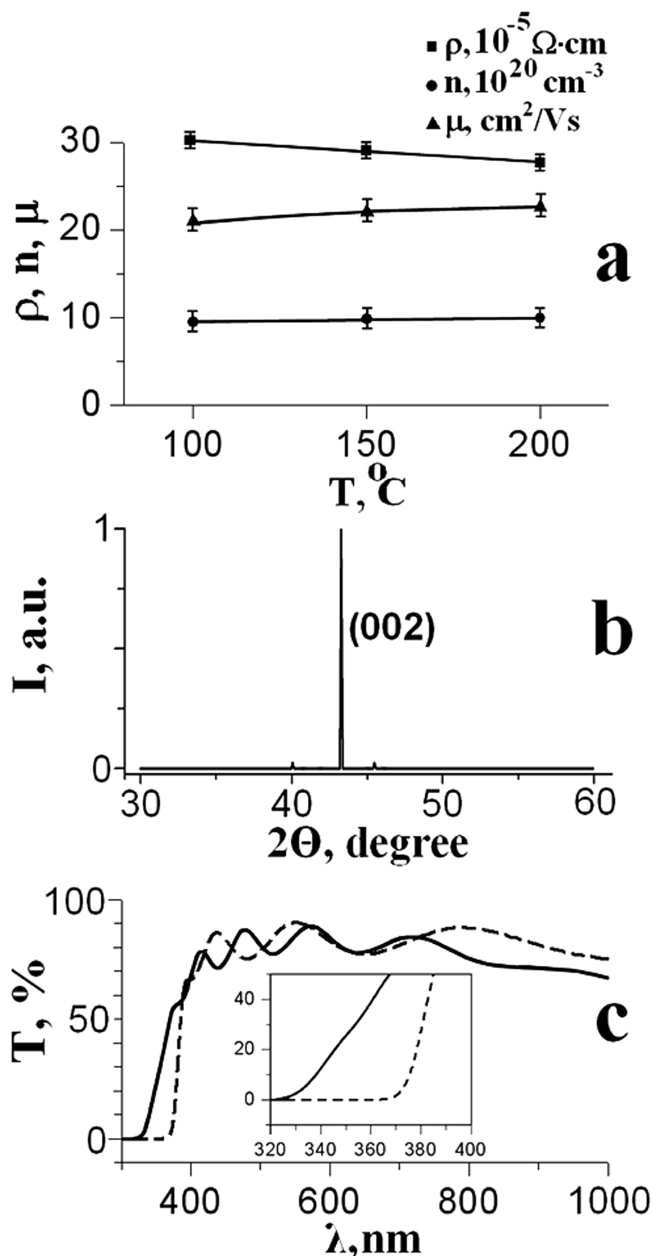

Fig. 7. Properties of ZnO thin films grown by magnetron sputtering of ZnO ceramics with 3 mol % Ga_2O_3: the main electrical parameters as a function of deposition temperature (a); XRD spectrum (b); transmittance spectrum (dotted line corresponds to the undoped film); the inset illustrates the short-wavelength edge of the spectrum (c).

highest temperatures, the $ZnCl_2$ molecules become sufficiently mobile and can also fly away from the surface.

The assumption that F contributes to the incorporation of an Al impurity into ZnO was made earlier without any thermodynamic calculations [25]. A similar improvement of the doping level in the presence of Cl is expected for other metallic impurities (Al, In, Cr, Sc, Y). This effect, as well as the optimization of the deposition process, opens up new prospects for the growth of highly conductive ZnO thin films at relatively low temperatures (25–100 °C).

5. Conclusions

Highly conductive uniformly doped ZnO:Ga:Cl ceramics with a high density of 5.31 ± 0.19 g/cm^3 and a high hardness of 2.0 ± 0.2 GPa

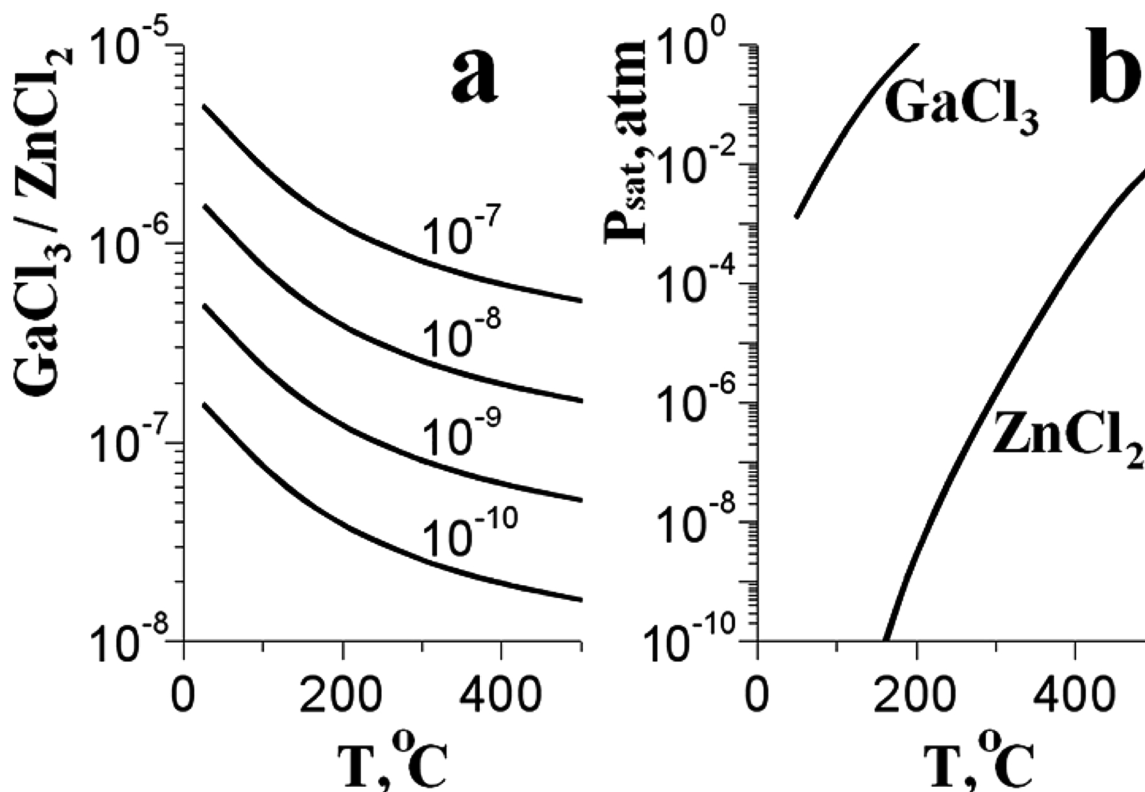

Fig. 8. (a) Value of $P(GaCl_3)/P(ZnCl_2)$ over $Ga_2O_3 + ZnO$ at a given $ZnCl_2^{\circ}$ pressure [atm] for various temperatures and (b) temperature dependence of the saturated vapor pressure of $GaCl_3$ and $ZnCl_2$ [18,26].

can be sintered by means of CVT reactions using HCl as the TA. This sintering method has the following advantages: (i) a low operating temperature of about 1000–1100 °C; (ii) there is no need to use expensive Ga_2O_3 dopant nanopowders (doping is conducted via CVT reactions involving $GaCl_3$ vapors having a pressure of 10^{-3} atm); (iii) the possibility of multiple re-sintering of sputtered and partially destroyed ceramics; and (iv) the absence of changes in the diameter of the ceramics after sintering. The solubility limit of the Ga_2O_3 dopant is estimated at about 3 mol %. At a higher doping level, the content of the $ZnGa_2O_4$ spinel phase in the studied material becomes significant. The most conductive ceramics with a resistivity of $(1.46 \pm 0.1) \times 10^{-3}$ Ω·cm can be obtained at 3 mol % Ga_2O_3. The presence of additional Zn vapors in the growth medium does not have a significant effect on the electrical properties of the ceramics. The ceramics remains highly conductive after annealing in a low vacuum (10^{-4} atm) at 600 °C.

ZnO:Ga:Cl ceramics can be used as magnetron targets to grow ZnO thin films with a resistivity of at least $(2.77 \pm 0.1) \times 10^{-4}$ Ω·cm (deposition temperature of 200 °C). Variation in the deposition temperature in a range of 100–200 °C does not affect the doping efficiency and the charge carrier concentration (10^{21} cm^{-3}). A model to interpret the improved incorporation of the Ga impurity into the ZnO lattice at low temperatures with the use of $GaCl_3$ vapors is proposed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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