



Effect of chlorine on the conductivity of ZnO:Ga thin films

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Introduction

Zinc oxide (ZnO) thin films have broad application prospects, in particular, in light-emitting, photoconductive, and thermoelectric devices.

The main requirements for these films are a low resistivity ($\leq 10^{-3} \Omega \cdot \text{cm}$) and a high optical transparency in the visible spectral range ($\geq 85\%$). The most typical donors for ZnO are B, Al, Ga, and In. Advantages of gallium are as follows: (i) it is less reactive and more stable to oxidation than Al; (ii) Ga and Zn atomic radiuses are similar (feature that provides a decrease in the deformation of the ZnO lattice even at a high doping level); and (iii) the solubility of Ga in ZnO can reach at least 4.5 at %.

A lot of studies were focused on the preparation of highly conductive ZnO:Ga thin films. Resistivity (ρ) of $3.8 \times 10^{-4} \Omega \cdot \text{cm}$ was achieved for films obtained by magnetron sputtering at 250 °C. Unfortunately, at lower deposition temperatures (~ 100 °C), these films, having a thickness of 300 nm, usually exhibit a higher resistivity of $(11 - 15) \times 10^{-4} \Omega \cdot \text{cm}$ due to a lower doping efficiency and charge carrier mobility. At the same time, low-temperature deposition (~ 100 °C) is required for manufacturing various devices. Lower sheet resistance and resistivity values can be achieved in relatively thick films having a higher crystallite size. For example, a resistivity of $2.8 \times 10^{-4} \Omega \cdot \text{cm}$ was obtained in 1100-nm-thick ZnO:Ga films. Typically, these films exhibit a relatively low transparency of $< 85\%$.

There are several methods to increase the conductivity of ZnO thin films. Excess Zn in the growth system (for example, sputtering ZnO:Ga:C composite targets) makes it possible to obtain films with a ρ value of about $2.5 \times 10^{-4} \Omega \cdot \text{cm}$ (300 nm, deposited at 300 °C); however, in the case of deposition at 100 °C, these films showed a significant concentration of unsublimated Zn and a low transparency. Ultraviolet stimulation of growing films decreases the ρ value by 25 % to $4.6 \times 10^{-4} \Omega \cdot \text{cm}$ (250 nm, 250 °C). Note that binary doping



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is also recognized as a promising way to increase the conductivity; for example, resistivities of 9.9×10^{-4} , 11.1×10^{-4} , and $8.1 \times 10^{-4} \Omega \cdot \text{cm}$ (~ 240 nm, 200°C) are reported for ZnO:Al, ZnO:Ga, and ZnO:Al + Ga thin films in. The electrical properties can be improved significantly by rapid thermal annealing (600°C in vacuum for 2 min); resistivity decreases to $4.4 \times 10^{-4} \Omega \cdot \text{cm}$ (290 nm) for ZnO:Al + Ga films. With an increase in the magnetic field strength at the target surface from 0.03 to 0.065 T, the resistivity of ZnO:Ga films can be decreased by 2 times, namely, to $2.2 \times 10^{-4} \Omega \cdot \text{cm}$ (300 nm, 250°C). Usually, this increase in the magnetic field strength is accompanied by a decrease in the sputtering area of targets. Authors of Ref. reported that the use of 10-nm-thick ZnO buffer layer, deposited via DC arc discharge ion plating, decreases the ρ value of ZnO:Al by 3 times to $4.6 \times 10^{-4} \Omega \cdot \text{cm}$ (500 nm, 200°C). Further optimization of the deposition angle can additionally decrease the resistivity of these films to $2.1 \times 10^{-4} \Omega \cdot \text{cm}$. Due to the fact that hydrogen interacts with the sputtered material and forms Zn excess in ZnO, the use of an Ar + H₂ mixture as a working gas decreases the resistivity of ZnO:Al films by 2 times to $13.7 \times 10^{-4} \Omega \cdot \text{cm}$ (120 nm, 200°C) [13]. In addition to cation dopants, anion dopants (F, Cl) can also act as shallow donors in ZnO. Co-doping with III-valence metals and halogens is also an effective approach. A decrease in the ρ value by 2 times to $2.9 \times 10^{-4} \Omega \cdot \text{cm}$ (350 nm, 200°C) is reported for ZnO:Al + F thin films compared with simple Al doping. The additional impurity (F) contributes to a better incorporation of the Al impurity into the ZnO lattice as shallow donors. This factor increases the free electron concentration, while the charge carrier mobility remains almost constant [17]. ZnO films doped only with F have a ρ value of $7.7 \times 10^{-4} \Omega \cdot \text{cm}$ and $5.3 \times 10^{-4} \Omega \cdot \text{cm}$ for 350 nm (room temperature deposition) and 790 nm thickness (300°C deposition), respectively.

Fluorine is a toxic and chemically aggressive substance; this feature complicates the use of F in magnetron systems and in high-temperature sintering of ZnO:F ceramic targets for magnetron sputtering. Less active chlorine should be more appropriate for semiconductor technology. Cl can form compensating interstitial defects (Cl_i) and shallow substitutional donors (Cl_O). However, Cl_i defects should have a rather large formation energy, and their concentration should be relatively low. ZnO films heavily doped with Cl can be obtained by chemical methods in Cl-rich solutions [18, 19]. The resistivity of $19 \times 10^{-4} \Omega \cdot \text{cm}$ is achieved for ZnO:Cl films with a thickness of 1600 nm (150°C annealing). These films can be used in stable solar cells. Unfortunately, many chlorides, in particular, ZnCl₂, are highly hygroscopic



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and volatile; these features limit their use as dopants in classical ceramic targets sintered in air. The chemical vapor transport (CVT) technique can be proposed as an alternative approach for sintering ceramics. A high pressure of doping gaseous species involved in CVT reactions can contribute to the formation of uniformly doped ceramics in the gas phase even at low sintering temperatures. Several transport agent mixtures based on HCl were proposed for an unseeded growth of CVT ZnO single crystals. Subsequently, these transport agents were proposed for sintering ZnO:Cl ceramics. Finally, uniformly doped ZnO:Ga:Cl ceramics with a resistivity of as low as $10^{-3} \Omega \cdot \text{cm}$ were successfully obtained using CVT. It was shown that these ceramics can be used to produce highly conductive ZnO thin films; however, a detailed analysis of properties of the films and the identification of optimum growth conditions have not yet been carried out.

Thus, the most conductive ZnO thin films obtained using a strong magnetic field, buffer layers, or co-doping with F have a ρ value in a range of $(2.1-2.9) \times 10^{-4} \Omega \cdot \text{cm}$ and an average transparency in a range of 90–94% [11, 12, 17]. The figure of merit (depending on the sheet resistance and average transparency (Sec. Advantages of co-doping with Cl. Effect of temperature on the properties of ZnO thin films)) reaches a value of 20–42 $\text{k}\Omega^{-1}$ at a deposition temperature of at least 200 °C. In the case of deposition at 100 °C, the figure of merit of these films is usually 2–3 times lower. The purpose of the present work is to search for alternative and independent methods for increasing the conductivity of ZnO thin films that are applicable at low deposition temperatures. One of these methods can be based on co-doping with chlorine. The object of this research is ZnO films obtained by magnetron sputtering of targets of a new type, sintered by the CVT method and doped with Ga and Cl impurities. This extensive study addresses the effect of all significant growth factors on the electrical properties of ZnO:Ga:Cl thin films, in particular, deposition temperature, film thickness, growth rate, background pressure, working gas pressure, preliminary slow-growing and undoped layers, stoichiometric deviation, and Ga and Cl concentrations. Changes in the growth rate, transparency in ultraviolet and visible spectral ranges, morphology, crystallinity, and crystallite size are also analyzed. A model taking into account various types of mobile gallium chlorides is proposed to elucidate the advantage of co-doping with Cl.