DOI: 10.54254/2755-2721/56/20240603

# Relationship between doped structure and properties of Zinc oxide film

**Zhouwei Ye**

Chemistry Jiangsu Normal University, Xuzhou, Jiangsu, 221116, China

1803092688@qq.com

**Abstract.** Overview of relevant research fields: Introduce the basic concepts and background of oxidizing thin films and doped materials. Discuss the characteristics, applications, and effects of doping on the performance of oxidizing thin films. Types and effects of doping elements: Introduce commonly used doping elements in oxidizing thin films, such as Al, Ga, Sn, etc. Discuss the effects of different doping elements on the properties of thin films, such as electrical, optical, and magnetic properties. Temperature and concentration effects: Exploring the effects of doping temperature and concentration on the properties of oxidizing thin films. Analyze the mechanisms and patterns of the effects of temperature and concentration on lattice structure, defect morphology, and carrier concentration. Application Fields and Prospects: Review the research progress of oxidative thin film doping in various application fields, such as optoelectronic devices, catalysts, sensors, etc. Looking forward to the future development direction and potential application fields of doping in oxidizing thin films. When writing a review, ensure accurate citation of relevant literature and analyze and discuss from multiple perspectives. In addition, pay attention to using concise and clear language to make it easy for readers to understand and obtain information. The most important thing is to ensure that the literature review complies with academic integrity and ethical standards, and adheres to citation norms.

**Keywords:** ZnO Film, Doping Properties, Crystal Structure.

## 1. Introduction

(ZnO) Zinc oxide film is a kind of material with a wide range of uses, raw materials are easy to obtain, high quality and low price, is a widely used film material with development potential that has been used in real life, and its properties will change with different doping components and preparation conditions. For a long time, the research on ZnO films has mainly focused on piezoelectric, conductivity, photoelectricity, gas sensitivity, and pressure sensitivity.

Optical properties: ZnO film in the range of visible light, visible light transmittance is high, this property can be used as a transparent solar cell electrode, but ZnO film in the ultraviolet and infrared spectrum range transmittance is relatively low.

Conductivity: There are intrinsic defects in ZnO films, and the gaps Zn atoms and O vacancies in its configuration are the reasons for the weak n-type conductivity of ZnO films. ZnO films generally have high resistivity and relatively poor conductivity.

Optoelectricity: ZnO film is a good photoelectric material, it has good photoluminescence characteristics. The research has been extended to its intrinsic luminescence, electroluminescence, etc., because it is easy to dope. Its conductivity can be enhanced by incorporating group III elements; It can also be incorporated with group V elements to give it a P-shaped structure. Improve its electroluminescence and other capabilities.

Gas sensitivity: ZnO film is a surface-controlled gas sensitive material with stable physical and chemical properties. It has the advantage of relatively high sensitivity to ethanol and other gases, but also has the disadvantage of poor selectivity to sensitive gases. The detection of a single gas can cause a significant obstacle.

Impurities and defects in materials have an extremely important impact on the properties of materials, especially for semiconductor materials. The intrinsic ZnO is naturally n-type, which is easy to dope with the donor. ZnO films are mainly conductive by point defects, and there are six main eigenpoint defects in the crystal lattice: oxygen gap (Oi), zinc gap (Zni), oxygen vacancy (Vo), zinc vacancy (Vzn), oxygen inversion (Ozn) and zinc inversion (Zno). Among them, Vo, Zni and Zno are donor defects, and Vz, Oi and Ozn are recipient defects. Among these six eigenpoint defects, donor defects Zn and Vo are relatively easy to form, and have been considered the main reasons for the n-type conductivity of intrinsic ZnO [1].

Among the advantages and disadvantages of ZnO films, many structures and properties that need to be improved can be adjusted and optimized by doping different elements, which is also the research trend and direction of ZnO films today. A large number of studies have reported that a variety of preparation techniques can be used to deposit ZnO thin films, such as magnetron sputtering (MS), chemical vapor deposition (CVD), and newly developed technologies in recent years - laser deposition (LD), sol-gel (Sol-ge1) and pulsed laser deposition technology (PLD), which have made considerable progress in the preparation of ZnO films.

To deposit thin films on temperature-sensitive substrates, ion-assisted deposition technology meets the conditions and has certain advantages. The vapor deposition technology and magnetron sputtering technology can prepare thin films with good quality and high repeatability. Doped zinc oxide films prepared by different technologies and different elements can meet different needs. By adjusting the experimental parameters, the ZnO film after donor doping can have good conductivity and visible light transmittance at the same time. For doped ZnO semiconductor materials, it can be seen from the resistivity formula $\rho = \frac{1}{en}\mu$, and the resistivity is affected by the combination of carrier concentration n and mobility $\mu$. In general, the introduction of doping elements increases the carrier concentration n. At low doping concentrations, carrier concentrations are approximately equal to doping concentrations.

## 2. Doping of group elements

There are many methods of donor doping of ZnO, among which one of the most commonly studied is to incorporate group III elements B, Al, Ga, In and Sc, Y, etc. to replace the position of Zn atoms to form a donor energy level and contribute an electron to participate in conductivity, the most widely used are group III elements Al, Ga, In.

### *2.1. Study on the properties of zinc oxide modified by Al doping*

Polycrystalline ZAO films have obvious c-axis preferred orientation and columnar growth, and substrate temperature and oxygen partial pressure have great influence on the transparent conductivity of ZAO films. When the doping concentration of aluminum ions is very low, it mainly exists in the crystal lattice in the form of gap ions, causing lattice distortion and reducing the crystallinity of the film. When the doping concentration reaches a certain value, aluminum ions replace zinc ions and begin to promote the optimal growth of crystals, and after exceeding a certain doping amount, aluminum ions are easy to accumulate at grain boundaries, hindering the growth of crystals.

The magnitude of the film resistivity is mainly determined by the concentration of carriers and the mobility. In the ZAO transparent conductive film, A l provides 1 electron for the alternative doping of Zn, which is the main source of carriers, and more doping atoms occupy the lattice position of Zn atoms,

DOI: 10.54254/2755-2721/56/20240603

resulting in the production of more carriers, therefore, the conductivity increases with the amount of doping. At the same time, the wavelength of the optical absorption edge will move towards the visible short-wave direction with the increase of substrate temperature, resulting in the phenomenon of "blue shift". This phenomenon can be explained as: it can be seen from the carrier concentration formula n∝-(E-Ed) in semiconductors, and n is inversely proportional to the difference between the conduction band bottom and the donor energy level; As the temperature rises, the carrier concentration increases, and the increased carrier fills the lower energy level in the conduction band, and makes the valence band electrons jump to a higher energy level in the conduction band, so that the absorption edge moves in the short-wave direction, that is, the Burst-ein-Moss effect. After doping, the crystallization order degree of ZAO film is improved, and the internal crystal defects are reduced, so that ZAO film not only has excellent electrical conductivity, but also is a transparent conductor with strong stability.

The main preparation process of ZAO film is pulsed laser deposition, spray thermal decomposition, chemical vapor deposition, radio frequency sputtering, DC sputtering, sol gel, etc., sputtering technology to prepare the film has the advantages of dense, uniform, strong adhesion, good repeatability, controllable composition, etc., is widely used in various process production processes, compared with the original ZnO film, under the same process conditions, AZO film than ZnO film diffraction peak higher and half height width is small, the comparison of the conductivity of the two is shown in Figure 1, The conductivity of the doped sample is increased by 6 orders of magnitude compared with the undoped sample, with a maximum of $2.3 \times 10^2\ \Omega^{-1} \cdot cm^{-1}$ [2]. The carrier concentration increases almost linearly with the increase of doping amount, however, after the doping concentration increases to a certain value, the doping atoms in the grain and grain boundary tend to saturate, and the excessive doping concentration leads to scattering of ionized impurities, so that the electron mobility of the film decreases.

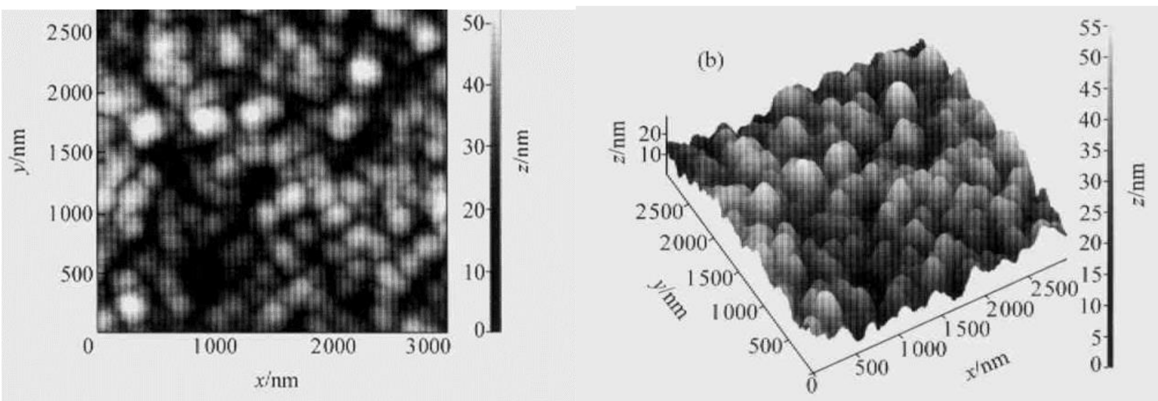


**Figure 1.** Atomic force microscope surface topography of ZAO film.

### 2.2. *Study on the properties of Ga-doped modified zinc oxide*

Ga atomic radius (0.126nm) and Zn atomic radius (0.135nm) are close, Ga-O bond (0.192nm) is also close to the Zn-O bond (0.197nm) bond length, even in the case of high doping concentration, the ZnO lattice distortion caused by Ga atom instead of Zn atom is relatively small, which is conducive to the incorporation of Ga and the improvement of the crystal quality of the film. As a doping element, Ga is conducive to the use of metal particle characteristics to suppress intrinsic defects such as oxygen vacancies in the active layer of pure zinc oxide thin film transistors, and realize the regulation of carriers. Gallium ions replace zinc ions as impurities, and a free electron is released in the conduction band at room temperature, which can effectively improve the conductivity of the device.

J. A. Sans et al. studied the thermal stability of the electroactive center of GZO by analyzing the X-ray absorption of Ga in Ga-doped ZnO films, and found that the Ga donor atom still showed good electrical activity after annealing at 800 °C under vacuum conditions, on the contrary, annealing in air at 400C led to a decrease of 4 orders of magnitude in GZO conductivity. When the structure and morphology of GZO films were explored under the spectrum. The morphology of GZO film will show needle-like, seed-like and granular structures, and the average grain size is between 5~20 nm. The highest mobility ($53\ cm^2/Vs$) with high carrier concentration was found under low laser pulse number irradiation (1800). Among them, the needle-like structure is more conducive to the optical enhancement of GZO film. Minimum resistivity ($3.5 \times 10\ Q \cdot cm$) with 80% transmittance. The film showed C-axis preferred orientation growth, and the average transmittance in the visible light range was greater than 90% [3]. Prepared by magnetron sputtering method, GZO film obtained the best photoelectric performance at 300℃, 0.2Pa and 180W. The highest conductivity of ZGO is $(1{\sim}2) \times 10^3\ \Omega^{-1} \cdot cm^{-1}$. The substrate temperature has a great influence on the structure of the GZO film, and with the increase of the substrate temperature, the crystallization orientation of the film changes, and a strong (002) preferred orientation peak will appear in the film at the substrate temperature of 250 ℃. The film thickness increases linearly with the sputtering time and sputtering power. The sputtering time is 15min, and the film structure is the best. When the sputtering pressure is 0.5Pa and the target base distance is 50mm, the structure of the film is the most perfect [4].

## 3. Doping of group IV elements

Another way is to incorporate group IV elements Si, Ge, Sn, Ti, Zr, etc. to replace the position of Zn atoms, contributing two electrons to participate in conduction

### *3.1. Study on the properties of Sn doped modified zinc oxide*

Semiconductor materials play an important role in monitoring toxic and harmful flammable gases and organic volatile liquids in the environment, such as HS, SO, CO, H, ammonia, natural gas, gasoline, ethanol, formaldehyde, etc. The pure zinc oxide film as a component in the gas sensor will cause some gases to cause relatively large interference to the detection of ethanol gas, and even cause working failure. In order to improve the gas sensitivity performance of zinc oxide film, some dopants are often added, and high ethanol gas detection sensitivity and good selectivity can be obtained by doping Sn and other substances in zinc oxide.

$Sn^{4+}$ has two more electrons than $Zn^{2+}$, which can increase the carrier concentration in ZnO; On the other hand, the radius of $Sn^{4+}$ (0.069nm) is similar to the radius of $Zn^{2+}$ (0.074nm), which does not cause large distortion of ZnO lattice when doped, and is easy to dope. Compared with the XRD pattern of pure ZnO film, the diffraction peak of Sn-doped ZnO film shifted to a small angle, indicating that Sn may exist in ZnO crystal as a gap atom.PL the spectral results showed that the defect concentration of ZnO samples increased significantly by doping Sn, and the gas sensitivity test results showed that this quadruped ZnO film with high defect concentration showed a good gas sensitivity response to ethanol gas at room temperature. After annealing the Sn-doped ZnO samples in air, their room temperature gas sensitivity disappeared, and it was speculated that the room temperature gas sensitivity of Sn-doped ZnO samples may be related to its high defect content [5].

The addition of Sn can also effectively improve the photocatalytic activity of ZnO. The molar ratio of different raw materials has a significant effect on its morphology, and with the increase of Sn doping, Sn-doped ZnO zinc oxide films can present different morphologies (granular, spherical and spinel). The reason for the analysis of its morphology change may be that the addition of Sn element in the reaction system affects the surface free energy during the crystal growth reaction. Sn doping significantly increases the near-ultraviolet absorption rate of ZnO film, which can be considered as an enhancement of infrared absorption or infrared reflection of ZnO film.

### *3.2. Exploration of the properties of Si-doped modified zinc oxide*

The valence band of ZnO is mainly determined by the O2p state, the energy level is deeper, and $SiO_2$ is deeper than the valence band of ZnO, which may make the valence band of ZnO move in the direction of low energy through Si doping, and at the same time, Si doping also provides useful information for the luminescence mechanism of ZnO visible region.

DOI: 10.54254/2755-2721/56/20240603

SZO film is n-type semiconductor, SZO film is polycrystalline structure, doped (002) diffraction peak moves to a large angle, with the increase of Si doping concentration, the carrier concentration of SZO film first increases and then decreases, mobility continues to decrease, resistivity continues to increase. The visible light transmittance of SZO film is above 85%, which is related to the good uniformity and low surface roughness of SZO film.

The surface roughness of Si-doped ZnO films becomes smaller, which is caused by the surface annealing of oxygen plasma. The SZO film is dominated by ultraviolet luminescence, and in the Raman spectrum, the 1-LO phonon is blueshifted, which indicates that Si may have been incorporated into the ZnO lattice. With the increase of doping concentration, the lattice quality decreases, but as the annealing temperature increases, the lattice quality increases. Since the band gap of SiO and SiO2 is larger than that of ZnO, according to the band clipping theory, Si incorporation will increase the band gap of ZnO. However, at the same time, the incorporation of Si enhances the luminescence in the visible region of ZnO and reduces the lattice quality. With the increase of annealing temperature, the band gap of doped ZnO films decreases. After annealing of the undoped ZnO film at 700 °C under oxygen atmosphere, the ultraviolet luminescence is enhanced, the visible luminescence is weakened, and the visible luminescence center is blueshifted, while the Si-doped ZnO film is also observed in the annealing process The visible luminescence center blue shift phenomenon is also observed, with the increase of Si doping concentration, the ultraviolet luminescence intensity becomes lower, the luminescence peak continues to shift blue, and the annealing temperature required for the blue shift of the visible luminescence center is also increased. This indicates that there is a strong interaction between the Si incorporated in ZnO and the deep energy level defects that produce the luminescence in the visible region of ZnO [6].

## 4. Common metal elements such as CuAg are doped

### *4.1. Exploration of the properties and structure of Ag-doped oxidizing films*

Ag-doped ZnO has the advantage that it is not easy to form interstitial donor impurities, and interstitial donor impurities are the main disadvantages of ZnO doping scheme of Li and other I. elements. Ag-doped ZnO films have significant strong ultraviolet luminescence characteristics. Ag-doped ZnO films can form various micro-nanostructures, thus producing many new properties. In addition, Ag nanoparticles have a strong surface plasma, which can make their surface substances strongly excited, so as to effectively adjust the electronic energy state structure of ZnO nanomaterials, change the surface state, and regulate their properties.

According to Scherrer's formula, it was found that the grain size of the film increased significantly with the increase of Ag doping concentration, and when the Ag doped atom fraction was 7%, the ZnO grain size in the film was the largest, about 50.9 nm. Ag elemental grain size is the smallest, about 30.6 nm. When the Ag doped atom fraction is 9%, the diffraction peak strength of the film decreases, the crystallinity becomes worse, and the ZnO grain size becomes smaller, which may be due to the inhibition of grain growth in the film when the Ag doping concentration is large. In addition, the diffraction peak of Ag-ZnO films was consistent with that of pure ZnO, and no other heteropeaks appeared, indicating that the doping process did not destroy the ZnO crystal structure.

With the increase of Ag doping concentration, the absorption peak intensity of the film around 370 nm gradually decreases, and a new absorption peak is generated at 380~450 nm, which is caused by the plasma resonance of nano-Ag particles in the film. The position of the resonance absorption peak is related to the size of the nanoparticles and the surrounding medium, and after doping with Ag, the transmittance of the film in the visible light range shows a downward trend, which may be caused by the absorption of Ag particles, but the transmittance of the Ag-ZnO film is above 85%, which has good optical properties [7].

Due to the addition of Ag, the conductivity of Ag-ZnO films is significantly better than that of pure ZnO films, and the conductivity characteristics of Ag-ZnO films are gradually enhanced with the increase of Ag doping concentration. ZnO conduction is mainly due to oxygen vacancies and interstitial zinc atoms, because Ag replaces $Zn^{2+}$, free electrons and gap Zn atoms are generated, which is conducive to the migration of free charge, so Ag doping reduces the resistance. When the Ag doped atomic fraction is 7%, the conductivity of the film is the best, and its conductivity is increased by about 200 times compared with the pure ZnO film. At this doping concentration, the ZnO grain size in the film is the largest, and the larger grain size helps the transport of electrons or holes in the film, which is also an important reason for the enhancement of conductivity. When the Ag doped atomic number fraction is 9%, the conductivity of ZnO film deteriorates, which may be due to excessive doping that Ag enters the ZnO lattice to form a solid solution, which hinders the migration of free electrons along the grain boundary and reduces the electron mobility.

With the introduction of Ag elements and the increase of doping concentration, Ag elements were formed in ZnO films, and resonance absorption peaks caused by Ag elemental particles appeared at wavelength 404 nm, and the conductivity of ZnO films was significantly improved, and the light transmittance of the films was above 85% in the visible light range. When the Ag doped atomic number fraction is 7%, the film conducts best, and its light transmittance in the visible range is as high as 90%.

### *4.2. Exploration of the properties and structure of Cu-doped oxidizing films*

In the photoluminescence (PL) spectrum, a blue light emission band of about 435 nm was observed, and the intensity of the light emission band was related to the amount of Cu doping and sputtering power. When the sputtering power was 150 w. Cu doping amount was 2.5%, a strong blue light bimodal appeared in the PL spectrum of the ZnO film, while when the sputtering power was 100 W and the Cu doping amount was 1.5%, a strong blue light peak at 437 nm (2.84 eV) appeared, and the latter had better orientation. The effects of doping amount and sputtering power on luminescence characteristics were also studied, and the mechanism of blue light luminescence of samples was discussed.

Since Cu ions come in Cu(+1) Cu(+2) forms, the Cu ion radius (0.096 nm) is larger than the ion radius of Zn (0.074 nm), and it mainly exists as substitute impurities in ZnO films, and the Cu ion radius (0.072 nm) is slightly smaller than the ion radius of Zn, and can exist simultaneously as substitute impurities and gap filled impurities in ZnO films. There may be Cu substitution, $Cu^{2+}$ substitution and Cu gap filling impurities in Cu-doped ZnO film, which affect the zinc vacancy and zinc gap filling defect concentration in ZnO film. When the Cu doping amount was 2.5%, the concentration of zinc vacancies and zinc gap filling defects in ZnO films increased at the same time, so a strong blue light bimodal was seen, and the blue light band was composed of multiple luminescent peaks, and the blue light band was derived from zinc vacancies and zinc gap filling defects.

The luminous intensity of blue light of ZnO film changes with the change of sputtering power, when the sputtering power is small (100W), it is easy to generate +1 valence Cu ions, and the ion radius is larger than the ion radius of Zn, and substitute impurities are formed in the film, resulting in an increase in zinc gap filling defects, so a strong blue light peak is observed in the PL spectrum. When the sputtering power is large (200W), it is easy to generate +2 valence Cu ions, which exist in the film in the form of substitute impurities and gap filling impurities, which are conducive to the generation of zinc vacancies and zinc gap filling defects. At 150W, there may be $Cu^{1+}$ and $Cu^{2+}$ Cu ions at the same time, so that there are a variety of impurities in the film, which affect the structure of the film, so the PL spectrum of the sample is blue band [8].

## 5. Conclusion and prospect

The doping of various elements of ZnO films has broad academic value, and ZnO films have considerable potential in the field of optoelectronic devices. In photoelectric conversion devices, ZnO films can be used as optical electrodes, electron transport layers or light absorption layers for devices such as solar cells, photodetectors and light-emitting diodes. Further research and optimization of the photoelectric characteristics of ZnO film doping is expected to improve the efficiency and stability of the device. At the same time, due to its doping to regulate piezoelectric performance and sensitivity, ZnO films can be used in pressure sensors, acoustic sensors, gas sensors and humidity sensors. Future research could focus on improving the sensitivity, selectivity, and reliability of ZnO thin-film sensors.

ZnO films also have potential in photocatalysis and energy storage. By doping and regulating the structure and surface characteristics of ZnO films, its photocatalytic activity can also be improved, and it can be used in the fields of water splitting, organic wastewater treatment and air purification. In addition, ZnO films can also be used in electrochemical energy storage devices such as supercapacitors and lithium-ion batteries. Although there are still many issues to be resolved and addressed, I remain optimistic and positive.

**References**

[1] ZHAO Yinzhong,LI Lin,XU Man,et al. Structure, Properties and Applications of ZnO Thin Films [J]. Lanzhou Institute of Physics, 2006, 24(4):529-531.

[2] YANG Bingchu, LI Xueyong, NIE Guozheng, et al. Optoelectronic properties of aluminum-doped zinc oxide film[J]. School of Physical Science and Technology, Central South University, Changsha, Hunan Province, Vol. 37, No. 6, December 2006

[3] Li Xia, Preparation and Application of GZO Transparent Conductive Film, Zhejiang University, January 2014

[4] Wang Xiaowei, Preparation of GZO Film and Its Optoelectronic Properties, Huazhong University of Science and Technology, January 2011

[5] XING Lanjun, CHANG Yongqin, SHAO Changjing Sn-doped ZnO Film with Room Temperature Gas Sensing Performance and Its Gas Sensing Mechanism[J]. Acta Physica Sinica, 2016, 097302

[6] YIN Dongmei Preparation and optical properties of Si-doped ZnO films. Northeast Normal University, June 2009

[7] Zhijun Chen, Gaoling Zhao, Xiaoxiao Ren, Sol_gel preparation and photoelectric properties of Ag/ZnO films State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou, Zhejiang. Volume 39 Supplement 2 August 2010

[8] PENG Xingping, LAN Wei, TAN Yong. Study on luminescence characteristics of Cu-doped zinc oxide film. Department of Physics, Lanzhou University[J], Lanzhou Journal of Physics, Vol. 53, No. 8, August 2004