OPTICAL PROPERTIES OF ZINC OXIDE DOPED WITH DIFFERENT DOPANT ATOMS

A Review

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Abstract: In this paper a review of provides information on the areas of application of zinc oxide, its advantages over other metal oxide semiconductors, and its possible use as an electrode in solar cells. The change of its optical properties, i.e., its optical transmittance, was considered when different input atoms were introduced. Zinc oxide doped with magnesium increases its optical conductivity, when sodium, aluminum and copper are added, its optical conductivity decreases. The future trends and perspectives of researchers on what kind of doping atoms should be doped to increase the optical transmittance are suggested at the end of this article.

Key words: metal oxide , ZnO thin film, .doped zinc oxide, optical properties

Currently, thin films based on transparent superconducting oxides have been widely studied due to their unique properties in optoelectronic devices such as light-emitting diodes, electronic paper displays, liquid crystal displays, touch panels, plasma displays, etc. . In particular, solar cells often require greater transparency than visible light to effectively utilize the entire solar spectrum. On the basis of metal oxide materials, it is possible to obtain multi-layered heterostructures that allow efficient use of solar radiation due to its different electrophysical properties and the width of the forbidden area, which covers a large part of the sunlight spectrum. In addition, the relatively simple and economical process of obtaining such heterostructures is important [1].

Metal oxide (M_nO_x)-based solar cells have the potential to solve some of the problems encountered in conventional solar cells, with excellent chemical stability and a fully oxidized perspective under environmental conditions. Due to the large amount of metal oxide that provides efficiency in production, M_nO_x is usually used as a functional layer in solar cells, for example, transparent conductive electrodes can be used in electrons (TiO_2, SnO_2, ZnO, Fe_2O_3etc) Since n-type metal oxides are of particular importance for the production of thin-film solar cells, indium-tin oxide (ITO) and doped zinc oxide (ZnO) are the main materials used for photovoltaic industrial production[2]. However, due to the high price of indium element in the market, it is urgent to obtain new necessary materials and properties for the industrial production of modern photovoltaic devices. In this context, thin films based on low-cost and high-performance transparent oxides are necessary and more in demand as a substitute for new optoelectronic devices. Among the many types of transparent conductive films, zinc oxide (ZnO) has attracted great interest.

Zinc oxide (ZnO) is a crystalline, n-type semiconductor belonging to the A_2B_6 group of compounds. Its band gap is about ~3.37 eV at 300K. The ZnO compound is a white crystal in the cold or at normal temperature, and when heated, the color of the substance changes: it turns yellow at about 250°C. This is explained by the decrease in the band gap and the shift from UV to blue in the absorption spectrum [3]. The main advantages for zinc oxide nanostructures include: ZnO growth can be carried out on a variety of substrates (including amorphous or flexible biological and degradable polymers); There are different synthetic ways to grow films, each of which has certain advantages; high volume electron mobility equal to the energy of ultraviolet light; the width of the prohibited area; high transparency; including unique properties such as room-temperature luminescence and high electron mobility, besides, ZnO has a controllable optical band gap that can be modified by changing composition, morphology, and volumes.

The optical properties of transparent conductive oxides formed by doping various chemical elements to zinc oxide (ZnO) were studied. Sodium, magnesium, copper and aluminum were considered as alloying elements. The optical conductivity of ZnO(MZO) doped with magnesium is shown below.

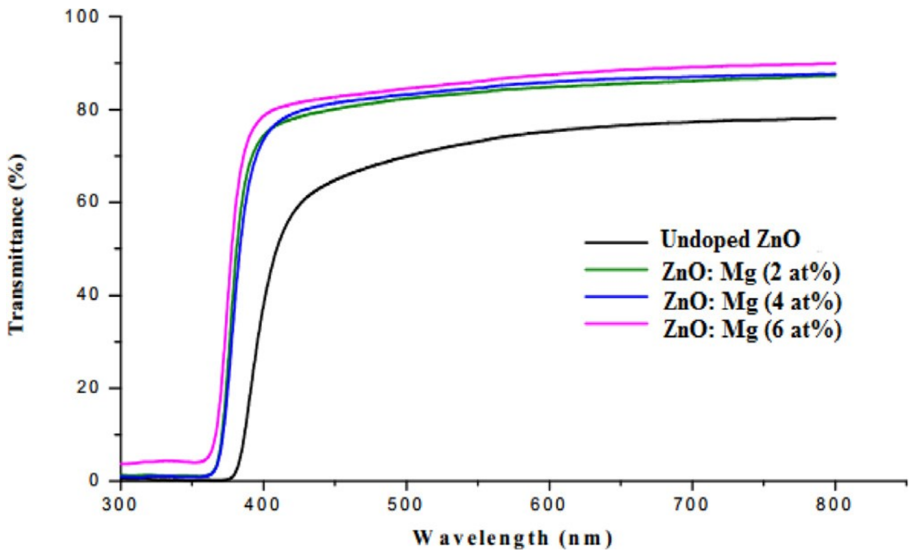

Figure 1. Optical transmittance spectra of the ZnO and MZO films with various Mg doping contents.[4]

The optical properties of MZO thin films were determined by transmission measurements in the range of 200–800 nm. The average thickness of the samples, measured by a stylus profilometer, is about 400 nm. It is shown in figure 1 surface emission spectra of ZnO and MZO thin films. Optical transmission increased to the visible light region. This depends on the increase in the concentration of Mg2+. The light transmittance of pure ZnO is 75%. value luminous emission of ZnO:Mg (2 at.%), ZnO:Mg (4 at.%) and ZnO:Mg (6 at.%)%) are 84%, 88% and 90%, respectively. It can be seen that with increasing doping, the absorption spectrum shifts to shorter wavelengths from 376 nm to 357 nm. The motion of the absorbing surface enhanced the optical transmission in the shorter wavelength region compared to pure ZnO thin films.[4]

Now let's look at the optical transmission of sodium doped ZnO

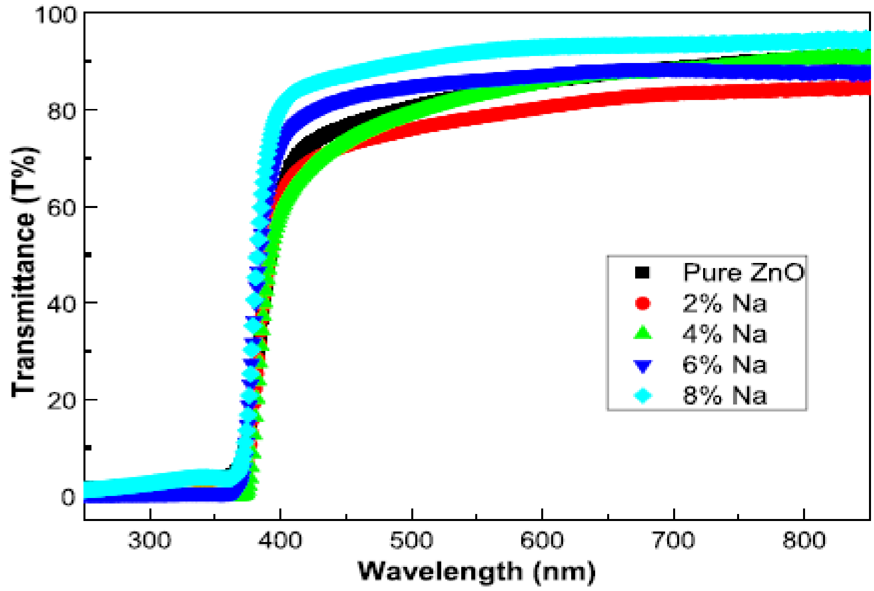

Fig. 2 Optical transmittance spectra of Na-doped and undoped ZnO films[5].

Fig. 2 shows the transmittance spectra of the undoped and Na-doped (2 at.%, 4 at.%, 6 at.%, and 8 at.%) ZnO thin films. It is obvious that the average transmittance of the films was above 80% in the visible range from 400 nm to 800 nm with sharp ultraviolet absorption edges in the UV region. A blue-shift of the ultraviolet absorption edge was found when the Na doping concentration was larger than 4 at.%.[5]

The optical conductivity of zinc oxide doped with aluminum changes as follows.

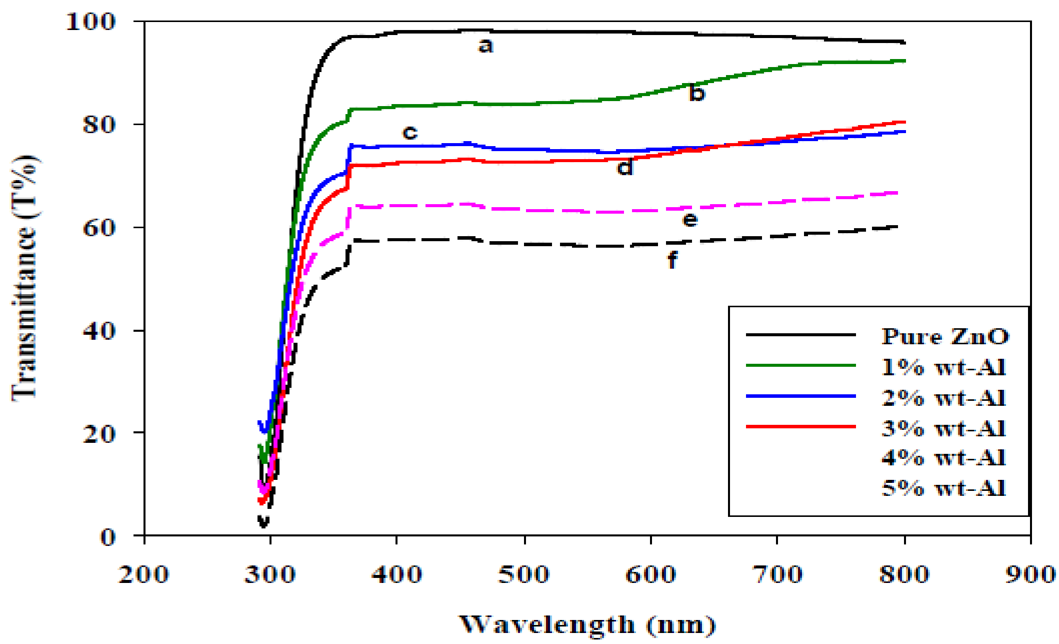

Figure 4: The optical transmittance spectra for the pure and Al-doped ZnO films deposited onto glass substrates: a-Pure ZnO, b- 1 % wt-Al, c- 2 % wt-Al, d- 3 % wt-Al, e- 4 % wt-Al, f- 5 % wt-Al[6]

Figure 4 shows the optical transmittance spectra obtained for the pure and Al-doped ZnO films deposited onto glass substrates. The optical transmittance of the films was obtained by averaging in the range 450 - 650 nm, as indicated by the vertical dashed lines. In the visible region the pure ZnO thin film had an optical transmittance of greater than 80% and by inserted the Al doping it is reduce to half with increase the Al doping to be 5% wt.

Copper doping zinc oxide changes as follows:

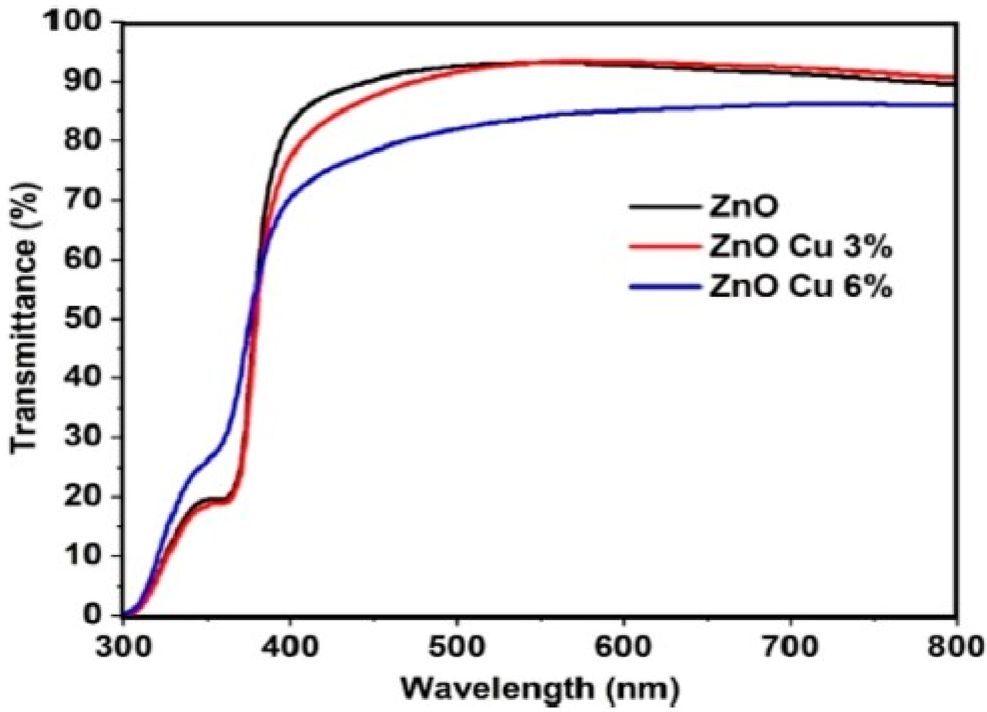

Figure 5. Transmittance spectra of pristine and Cu-doped ZnO films.[7]

ZnO is a direct band gap conductor, and its band gap can be easily determined by measuring the direct transition between conduction and valence bonds. Figure 5 shows the optical emission of the deposited samples measured at a wavelength of 300–800 nm using a UV spectrophotometer. All deposited films exhibit intense optical transmittance within the visible spectrum. For a transparent conducting oxide material, high transmittance is an important property that can reveal the morphological homogeneity and crystalline quality of the deposited films for the optical applications. The optical transmittance in Cu doped ZnO thin films is smaller than pristine ZnO, which may be due to the increase of absorbing and scattering centers with the incorporation of Cu^{2+} ions. The Cu 3d orbital is much shallower than the Zn 3d orbital, and when a Cu atom occupies a Zn site inside the ZnO lattice, it introduces two strong effects: first, the strong d−p interaction between Cu and O moves O 2p up, which narrows the direct fundamental energy gap, and second, the Cu 3d orbital creates impurity bands above the ZnO valance band. These impurity levels act as a strong absorption site in the UV−visible regime and are hence responsible for the decreases in transmittance in doped films[7]

Parameters of metal oxide films doped with various impurities

Table 1

№	Sample	Concentration of doping elements, mol,%	Crystallite size, nm	Wave length nm	Optical transmittance %	Optical band gap energy, E_g, eV
1	ZnO				75-80	3.37
2	Zn:Mg	2,4,6	19,24,28	376-357	84,88,90	3.20; 3,43
3	Zn:Na	2,4,6,8 .	50	300-600	< 80%	3,25; 3,20; 3.19; 3,26
4	Zn:Al	1,2,3,4,5	27, 12, 7	375	<75	3,408;3.404;3,35;3,32
5	Zn:Cu	3,6	~280	350-800	< 80%	3.25; 2.87; 2.31

Looking at the table, we can see that for all samples, the transmittance increased from 84% to 90% and the bandgap also increased from 3.20 to 3.43 (eV).

This concludes that the film is suitable for use in optoelectronic devices. A decrease in optical transmission and bandgap is observed with increasing concentration of samples doped with sodium, aluminum, and copper

Conclusions

From these serial experiments one may realize that it is likely to produce various metal doped thin film structures which might inhibit very interesting optical properties in the area of photonics. It is possible to change the optical conductivity, electrical properties, and chemical stability of zinc oxide doped with different input atoms. We cannot speculate about the application of optoelectronics, sensors or photovoltaics by optical conductivity alone. We still need to conduct a lot of research in this regard.

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