EFFECT OF ZnS AND CdS ON SOME PHYSICAL PROPERTIES OF MgO FILMS[†]

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This article reports on the fabrication and characterization of MgO nanostructured films and the effect of ZnS and CdS on their structural, optical, and electrical properties. The MgO, MgO: ZnS, and MgO: CdS thin films were deposited using a Chemical spray pyrolysis technique onto glass substrates at 673 K. The XRD patterns revealed that the MgO thin films had a preferred (111) orientation with a pure cubic crystalline structure, while the ZnS and CdS layers had a hexagonal structure. The FE-SEM images showed that the MgO films had a nanostructured morphology with an average particle size of ~50 nm. The UV-Vis spectroscopy results showed that the addition of ZnS and CdS layers to the MgO films resulted in a shift in the absorption edge towards the visible region of the electromagnetic spectrum, indicating an improvement in their optical properties. These findings suggest that the MgOZnS and MgOCdS films could have potential applications in optoelectronic devices.

Keywords: MgO films; Doping Effect; ZnS; CdS; Chemical spray pyrolysis; Physical properties PACS: 73.20.At, 78.20.-e, 77.55.-f

INTRODUCTION

Magnesium oxide (MgO) thin films have been studied for their potential use in a variety of applications, including as a dielectric material for microelectronic devices [1,2], To improve the performance of these devices, it is often necessary to introduce dopants into the MgO film. Doping involves introducing impurity atoms into the lattice structure of the MgO film to modify its electrical properties [3,4], Commonly used dopants for MgO include boron, phosphorus, and aluminum. These dopants can be introduced into the film during growth by adding them to the source material or by using ion implantation techniques. The effects of doping on the electrical properties of MgO thin films depend on both the type and concentration of dopant used. Generally, boron doping results in an increase in conductivity while phosphorus and aluminum doping results in a decrease in conductivity [5,6]. Magnesium oxide (MgO) thin films can be used to dope ZnS and CdS semiconductor materials. This doping process involves depositing a thin layer of MgO onto the surface of the ZnS or CdS material. The MgO acts as an acceptor dopant, meaning that it can donate electrons to the semiconductor material, thus increasing its conductivity [7,8], This process is often used in optoelectronic devices like solar cells. By doping ZnS and CdS with MgO, it is possible to improve their electrical properties, making them more suitable for use in these types of devices [9,10]. Chemical spray pyrolysis is a technique used to deposit thin films of semiconductor materials such as ZnS and CdS onto substrates. This technique involves spraying a solution of the desired material onto the substrate, followed by heating the substrate in an oven to evaporate the solvent and decompose the material into its constituent elements [11,12], The resulting thin film is then annealed at high temperatures to improve its crystallinity and electrical properties. Doping CdS and ZnS with magnesium oxide (MgO) can be achieved using chemical spray pyrolysis by adding MgO to the solution before spraying it onto the substrate, The MgO will then be incorporated into the thin film during pyrolysis, resulting in a doped semiconductor material [13], The doping concentration can be controlled by adjusting the concentration of MgO in the solution, as well as by varying other parameters such as temperature and time[14,15]. The goal of this research is to study the effect of ZnS and CdS on MgO films on the structural, optical, and electrical properties, The research will focus on understanding the influence of doping on the XRD, Energy gap, absorption coefficient, refractive index, and electrical conductivity of the thin films.

EXPERIMENTAL PART

Spray pyrolysis was used to deposit MgO,(MgO: ZnS), and (MgO: CdS) films. Magnesium chloride (MgCl₂.6H₂O), zinc nitrate (Zn(NO₃).6H₂O), cadmium chloride (CdCl2.6H₂O), and thiourea (CH₄N₂S) dissolved in distilled water with molarity (0.1M). (MgO) doped with 8% (ZnS) and (CdS). The chemical solution was sprayed onto glass substrates at 673K using a 1.5 bar compressor. The structural characteristics were determined using X-ray diffraction, field emission scanning electron microscopy, and An ultraviolet-visible (UV-Vis) spectrophotometer was used to measure the optical characteristics. and Hall effect measurement was used to determine the electrical properties.

RESULTS AND DISCUSSION

Figure (1) shows the X-ray diffraction patterns of (MgO) films doped with (CdS) and (ZnS). Table (1) shows the values of the diffraction angles, the width of the mid-peak, the crystal size, and the interlayer distances separating the

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crystalline levels. And Miller coefficients for (MgO) film, (Mg: 6%CdS) and (Mg: 6%ZnS) films respectively. The results showed that the films have a polycrystalline structure and obtain magnesium oxide (MgO) with a pure cubic crystalline structure and that the spectrum of magnesium oxide matches the standard spectrum (JCPDS 074-1225) with a crystalline level (Fm- 3m no.225) and crystal dimensions (a = b = c = 4.22 °A), while the angle values were ($\alpha = \beta = \gamma = 90$ °) [16], and after the doping process (6%) of cadmium sulfide (CdS), another hexagonal crystalline phase appeared. (JCPDS 077-2306)) with crystal dimensions (a = b = 4.136 °A and c = 6.713 °A) and angles ($\alpha = \beta = 90$ ° and $\gamma = 120$ °) [17], and this phase is more clear and crystallized with the doping. The figure (Fig. 1) shows that doping with zinc sulfide (ZnS) resulted in a fall in intensity and an increase in the width of the diagnostic peaks. This is due to (Mg) ion substitution with sulfur and zinc ions (S⁻² ions Zn⁺² and), ion diffusion within the crystal lattice of magnesium oxide (MgO), and the appearance of new peaks after doping, indicating the formation of (ZnS) a hexagonal Crystal Structure with (a=b = 3.82 Å, c = 6.25 Å) and ($\alpha=\beta=90^\circ$, $\gamma=120^\circ$), consistent with the standard spectrum (JCPDS 003-7393) [17,18].



Figure 1. XRD MgO films doped with (CdS) and (ZnS).

Table (1): Some crystal parameters of MgO before and after doping with (6 %) from ZnS and CdS.

Samples	20 (deg) Experimental	20 (deg) Standard	FWHM (deg)	Crystallite Size (nm)	dhkl (Å) Experimental	dhkl (Å) Standard
	<u>36 85</u>	36.86	<u>(ucg)</u> 0.94	9 30	2.43	2.43
MgO	42.77	42.82	0.55	16.19	2.11	2.13
8-	62.19	62.16	1.15	8.42	1.49	1.49
	78.63	78.44	0.40	26.80	1.21	1.21
	36.74	36.86	0.55	15.86	2.44	2.43
MgO: ZnS	42.74	42.82	0.39	22.62	2.11	2.11
C	61.94	62.16	0.31	30.71	1.49	1.49
	78.72	78.44	0.19	55.87	1.21	1.21
	36.94	36.86	0.29	29.62	2.43	2.43
	42.90	42.82	0.24	36.22	2.10	2.11
MgO: CdS	62.16	62.16	0.48	20.17	1.49	1.49
	24.94	24.80	0.59	14.38	3.56	3.58
	26.59	26.50	0.29	28.87	3.34	3.35
	28.17	28.18	0.39	21.72	3.16	3.16

The Energy Dispersion X-ray Analysis (EDX) in Fig. 2 and Table 2 shows the presence of MgO, MgO:ZnS, and MgO:CdS. Figure 2 describes the investigation of the morphology and surface structure of different films made of magnesium oxide (MgO) doped with different materials, such as zinc sulfide (ZnS) or cadmium (CdS). The investigation was carried out using a field emission scanning electron microscope (FE-SEM), The addition of zinc sulfide (ZnS) or cadmium (CdS) to a magnesium oxide (MgO) film can significantly impact the particle size of the resulting film. This is because the dopant material can affect the growth and formation of the film during the deposition process, leading to changes in the size and distribution of the particles. For example, the addition of ZnS to a MgO film can result in the formation of smaller particles with a more uniform size distribution, as the ZnS can act as a nucleation site for MgO growth [19, 20]. On the other hand, adding CdS can lead to the formation of larger particles due to the interaction between CdS and MgO during the deposition process, These changes in particle size can have significant implications for the properties and performance of the film, as demonstrated in previous studies [21, 22, 23].

Element	Weight %	Atomic %	
Mg	50.62	40.28	
Ō	49.38	59.72	
Total	100	100	
Mg	47.07	38.59	
Zn	4.51	1.38	
S	0.46	0.28	
0	47.96	59.75	
Total	100	100	
Mg	40.94	31.96	
Cd	1.74	0.29	
S	0.42	0.25	
0	56.90	67.50	
Total	100	100	

1 2 3

Figure 2. 1- FE-SEM and EDX of MgO films, 2- MgO:ZnS films, 3- MgCdS films.

The transmittance and reflectance of MgO films doped with CdS and ZnS can vary depending on the type and concentration of the dopant. Generally, the addition of dopants to MgO films can affect their optical properties, such as their transmittance and reflectance, Studies have shown that the addition of ZnS to MgO films can decrease their transmittance in the visible region, due to the larger particle size and distribution between the particles [24,25]. On the

Table (2): The Elements of MgO, MgO:ZnS and MgO:CdS from EDX

other hand, the addition of CdS can decrease the transmittance of MgO films, especially at shorter wavelengths, due to the formation of larger particles [26,27]. Reflectance measurements also depend on similar factors, and studies have shown that the addition of ZnS to MgO films can increase their reflectance in the ultraviolet region, while the addition of CdS can decrease their reflectance [28,29].



Fig. 3. Transmittance and Reflectance of MgO films doped with (CdS) and (ZnS).

The absorption coefficient and energy gap of MgO films doped with CdS and ZnS are important optical properties that can be affected by the type and concentration of the dopants, as well as the thickness of the film. Studies have shown that the addition of CdS and ZnS to MgO films can result in a decrease in the energy gap, due to the smaller particle size and the increase in the number of defects in the film [30,31]. This decrease in the energy gap can also lead to an increase in the absorption coefficient of the film. The relationship between the energy gap and absorption coefficient can be described by the Tauc plot, which is a method used to determine the optical properties of materials based on their absorption spectra [32]. The Tauc plot shows a linear relationship between the square of the absorption coefficient and the photon energy for direct bandgap materials, while indirect bandgap materials show a nonlinear relationship [33].



Figure 4. The Absorption coefficient and Energy gap of MgO films doped with (CdS) and (ZnS).

The refractive index and extinction coefficient are important optical parameters that can be used to characterize the optical properties of thin films. MgO films doped with CdS and ZnS have been shown to exhibit interesting changes in their refractive index and extinction coefficient due to the incorporation of dopant atoms into the MgO lattice. Studies have demonstrated that the addition of ZnS and CdS to MgO films can increase the refractive index of the film due to the formation of smaller nanoparticles with a higher degree of order, which leads to a greater degree of light confinement within the film [30-33]. The relationship between the refractive index and the amount of light reflected from a surface is such that higher refractive indices correspond to more reflection. This connection is expressed in equation (1) [34] :

$$\mathbf{n}_{o} = \left[\frac{(1+R)^{2}}{(1-R)^{2}} - (k_{o}^{2} - 1)\right]^{\frac{1}{2}} + \frac{(1+R)}{(1-R)}$$
(1)

The extinction coefficient of MgO films doped with CdS and ZnS can also be affected by the type and concentration of the dopants. The addition of ZnS and CdS to MgO films can increase the extinction coefficient due to the presence of larger particles with a higher degree of light scattering [3,4]. To determine the extinction coefficient (ko), equation (2) can be used [35].

$$k_{o} = \frac{\alpha \lambda}{4\pi}$$
(2)

The refractive index and extinction coefficient of MgO films are shown in Figure (5).



Figure 5. Refractive index and Extinction Coefficient of of MgO films doped with (CdS) and (ZnS)

The dielectric constant of a material is typically given by a complex quantity, with a real part (ϵ r) and an imaginary part (ϵ i) that relate to the material's ability to store and dissipate energy in an electric field, respectively. Equations (3) and (4) establish a relationship between the behavior of the real dielectric constant and the refractive index, as well as the imaginary dielectric constant and the extinction coefficient[36].

$$\varepsilon_{\rm r} = n_{\circ}^2 - k_{\circ}^2 \tag{3}$$

$$\varepsilon_{i} = 2n_{\circ}k_{\circ} \tag{4}$$



Figure 6. The real and imaginary part of the dielectric constant of MgO films doped with (CdS) and (ZnS).

MgO films doped with CdS and ZnS have been shown to have changes in their electrical properties . After studying Hall effect measurements of (MgO) thin films doped with ZnS and CdS at a 6% ratio, it was discovered that both types of films had negative charge carriers, as evidenced by the negative Hall coefficient (RH). This finding is consistent with previous research [36], The resistivity values of all films were observed to be high, with the films doped with ZnS and

CdS exhibiting the highest values. These high resistivity values are attributed to defects in the crystal structure of the film, which hinder the movement of charge carriers [37].

Samples	Concentration (cm) ⁻³	Hall Coefficient Rh (m ² /C)	Conductivity (Ω.cm) ⁻¹	Resistivity (Ω.cm)	Mobility (cm²/v.s)
MgO	2.584x10 ⁶	2.416x10 ⁷	1.035x10 ⁻⁵	9.662x10 ⁴	2.500×10^{2}
MgO:ZnS	4.325x10 ⁷	-2.886x10 ⁶	5.337x10 ⁻⁷	1.874×10^{7}	1.540×10^{1}
MgO:CdS	4.953x10 ⁶	-3.781x10 ⁷	1.309x10 ⁻⁵	7.638x10 ⁴	4.950×10^{2}

Table 2. Electrical Properties of MgO, MgO:ZnS, MgO:CdS Films.

CONCLUSION

The structural and optical properties of magnesium oxide (MgO) films can be significantly influenced by the incorporation of zinc sulfide and cadmium sulfide, These compounds, when added to MgO films, can cause noteworthy changes, including an increase in the refractive index, a reduction in the band gap, and an elevation in the optical absorption coefficient, Various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible spectroscopy, and Electrical Properties have been employed in several studies to investigate these effects, The findings conclusively demonstrate the substantial impact of zinc sulfide and cadmium sulfide additions on both the structural and optical characteristics of MgO films, These findings hold promising potential for applications like antireflective coatings and other optoelectronic devices.

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ВПЛИВ ZnS TA CdS НА ДЕЯКІ ФІЗИЧНІ ВЛАСТИВОСТІ ПЛІВОК MgO Н.А. Хассан^а, В.Х. Альбанда^ь, М.Х. Аль-Тімімі^а

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У цій статті повідомляється про виготовлення та характеристику наноструктурованих плівок MgO та вплив ZnS i CdS на їхні структурні, оптичні та електричні властивості. Тонкі плівки MgO, MgO: ZnS i MgO: CdS були нанесені за допомогою техніки піролізу хімічним розпиленням. на скляні підкладки при 673 К. Рентгенограми показали, що тонкі плівки MgO мають переважну (111) орієнтацію з чистою кубічною кристалічною структуров, тоді як шари ZnS i CdS мають гексагональну структуру. Зображення FE-SEM показали, що плівки MgO мають наноструктуровану морфологію із середнім розміром частинок ~50 нм. Результати УФ-видимої спектроскопії показали, що додавання шарів ZnS i CdS до плівок MgO призвело до зміщення краю поглинання у бік видимої області електромагнітного спектру, що вказує на покращення їх оптичних властивостей. Ці знахідки свідчать про те, що плівки MgOZnS i MgOCdS можуть мати потенційне застосування в оптоелектронних пристроях. Ключові слова: *плівки MgO; donine ефект; ZnS; CdS; хімічний розпилювальний піроліз; фізичні властивост*ії