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Complete List of Authors:	Güney, Harun; Agri Ibrahim Cecen Universitesi, İSKENDERÖĞLU, Demet; Ataturk Universitesi, Eastern Anatolian High Technology Applications and Research Center
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Characterization of MgO: Cd thin films grown by SILAR method

Harun GÜNEY^{1*}, Demet İSKENDEROĞLU²

¹*Vocational School, Department of Electric and Energy,
Ağrı İbrahim Çeçen University, Ağrı - Turkey*

¹*Central Application and Research Laboratory (MERLAB),
Ağrı İbrahim Çeçen University, Ağrı – Turkey*

²*Pasinler Vocational School, Departments of Electronics and Automation,
Atatürk University, Erzurum-Turkey*

²*Eastern Anatolian High Technology Applications and Research Center (DAYTAM),
Atatürk University, Erzurum-Turkey*

Abstract

The undoped and 1%, 2% and 3% Cd doped MgO nanostructures were grown by SILAR method on the soda lime glass substrate. X-ray diffractometer (XRD), ultraviolet–visible spectrometer, scanning electron microscope (SEM), photoluminescence (PL), X-ray photoelectron spectroscopy (XPS) measurements were taken to investigate Cd doping effects on the structural, optical and morphological properties of MgO nanostructures. XRD measurements show that the samples have cubic structure and the planes of (200), (220) of MgO and (111), (200) and (220) of CdO. It was observed that band gaps increase with rising Cd doping rate in MgO thin film. The surface morphology of samples demonstrates that MgO nanostructures have been affected by the Cd doping. PL measurements show that undoped and Cd-doped MgO thin films can be radiate visible emission region.

* Corresponding author: Agri Ibrahim Cecen University, Vocational School, Department of Electric and Energy, Agri 04100, Turkey, Tel. +90 472 215 7315, e mail: harunguney25@hotmail.com

1. Introduction

In recent years, undoped and doped MgO nanoparticles, thin films and bulk crystals have been extensively studied by scientists due to their wide application areas such as bactericide, refractory materials, transparent electrical devices [1, 2]. Especially doping in MgO is performed to improve some of the features highlighted and some important features of MgO can be controlled in several studies [2-6]. Also, doped and undoped MgO is grown by different methods in the literature such as sol-gel, solution combustion, chemical co-precipitation, sputter, electrodeposition method and so on [2, 3, 6-8].

According to the method, MgO thin films exhibit different structural, morphological and optic properties. The optically characterized intrinsic oxygen, magnesium ion vacancies originate PL emission in the blue region at room temperature while extrinsically exhibiting red emission by doping [9-11]. The MgO thin film can be emitted to different PL emission at various wavelengths in the visible region by doping.

In this study, Cd-doped MgO thin films were grown by the SILAR method, which was not studied previously. MgO thin films were researched optical, morphological and structural effected by 1%, 2% and 3% Cd dopant.

2. Experimental

The undoped and Cd doped MgO thin films were grown on soda lime glass substrates by the SILAR method. The glass substrate has been cleaned to remove any surface contamination. As a cleaning procedure, the glass substrate was cleaned in an ultrasonic cleaner for 300 s diluted sulphuric acid (1:5 v/v) and for 300 s and deionized water (DI) water, respectively. As is known, the binary and ternary compound semiconductors are performed with the SILAR method, usually with cationic and anionic precursors. In this study, the cationic precursor was made 0.1 M magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$) and different molar ratio cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$). These molar ratios of $\text{Cd}(\text{NO}_3)_2$ are 1%, 2%, 3%, respectively. The anionic precursor is DI water consists of an adjusted pH 11.5 by ammonium hydroxide (29%) solution. During the experiment, both cationic and anionic precursors were kept at about 90 °C. The substrate was immersed in the cationic precursor for 30 s and the anionic precursor for 30 s. All procedures were repeated for 20 cycles. For MgO formation, the undoped and Cd doped MgO thin films were annealed in atmospheric air at 400 °C temperature for 3600 s.

The thickness of thin films, which is a significant parameter in thin film studies, has been calculated by the gravimetric weight difference method and the thicknesses of all samples are approximately 800 nm [12].

3. Results and discussions

3.1. XRD analysis

The XRD measurements were taken for examining the Cd dopant effect on the MgO crystal structure and are shown in Fig. 1. In Fig. 1, all thin films have around 43° (002) and 62° (220) peaks belonging to the cubic structure MgO thin film according to ICSD card number 00-45-

0946. Cd doped MgO thin films which are more apparent especially in the 2% and 3% samples have around 33° (111), 38° (200) and 55° (220) peaks belong to the cubic structure CdO thin film according to ICSD card number 03-065-2908. This CdO formation may be that Cd ions fit into the structure and form CdO in some parts of the MgO structure. It is thought that the two structures are cubic so that this situation may be contributing to the formation of the CdO structure in MgO. The undoped and Cd doped MgO thin films have the dominant peak (200) plane and the other prominent peak (220) plane.

The inter-planer distance (d) of undoped and Cd doped MgO thin films are calculated by Bragg's law,

$$n\lambda = 2d\sin\theta \quad (1)$$

where, n equals to 1, λ is the the wavelength of the X-ray beam ($\lambda=1.5406$), and θ is the diffraction angle dominant and other peaks. The d values of undoped and MgO thin films are shown in Table 1 and conform to approximately with standard values of MgO (according to ICSD card number 00-45-0946 $d_{200}=2.106$ and $d_{220}=1.489$).

For undoped and Cd doped MgO thin films, the particle size (D) were performed by Debye-Scherrer formula,

$$D = \frac{0.94\lambda}{\beta\cos\theta} \quad (2)$$

where β is the full width at half maximum (FWHM) of the diffraction, θ is the half of angle of the observed peak. The calculated D results are shown in Table 1. Table 1 shows that the D values of undoped MgO thin films have significantly changed with the Cd dopant. This may be due to defects oxygen and/or Cd in the structure.

The lattice constant (a) and volume of the unit cell (V) for cubic undoped and Cd doped MgO thin films calculated from (200) which is the main peak of the XRD results data using the following Eq. (3) and (4) [13],

$$d = \frac{a}{\sqrt{(h^2+k^2+l^2)}} \quad (3)$$

$$V = a^3 \quad (4)$$

where h , k and l orientations of peaks. The a and V of undoped and Cd doped MgO thin films are demonstrated in Table 1. In Table 1, a values are 4.2396, 4.2436, 4.2399, 4.2302 Å and V

values are 76.2045, 76.4183, 76.2207, 75.6956 Å³ respectively. The calculated a and V values of undoped and Cd doped MgO are good matches with $a=4.2112$ Å and $V=74.68$ Å³ the standard data of ICSD standard card number 00-45-0946. So it can be said that the Cd dopant does not seriously affect a and V values of the MgO structure.

3.2. Adsorption and transmittance analysis

Fig. 2a shows undoped and Cd doped thin films absorbance measurements and photographs of samples as well as Fig. 2b shows transmittance measurements. Absorbance measurements do not show a significant change, as seen in Fig. 2a. Transmittance measurements show a decrease in transmittance with Cd dopant compared to undoped MgO thin film. With the Cd dopant, the sample changed color or even orange. As a result, the decrease in transmittance may be explainable the result of XRD in the structure. It can be considered that the source of the change in the 1% Cd doped MgO thin film is originated from Cd ions, and in the 2% and 3% Cd doped MgO thin films is originated from CdO according to XRD results. The reduction in transmittance in the oxide compounds is an indication of the increase in oxygen defects in the structure. Thus, it can be said that the decrease in transmittance is caused by the increase in the number of oxygen defects in the MgO [14]. The calculated band gap (E_g) of undoped and Cd doped MgO thin films are shown in Fig 3. The calculated E_g of MgO thin films decreased with the Cd dopant but increased as the amount of Cd increased. This blue shift may be the result of The Moss-Burstein effect.

3.3. SEM analysis

Fig. 4 show SEM photographs, one of the essential indicators in interpreting some properties of the samples, of undoped and Cd doped MgO thin films magnified 20,000 (a, c, e, g) and 10,000 (b, d, f, h) times. The change in surface morphology of MgO with the Cd dopant is evident. The Cd dopant changed the grain size as well as the homogeneity in the surface. This situation is supported by the XRD results as seen in Table 1.

3.4. PL analysis

Fig. 5 shows the PL measurements of undoped and 1%, 2% and 3% Cd doped MgO thin films taken at room temperature. In Fig. 5, the undoped MgO thin film has the peak observed at 464 nm (2.67 eV) at the blue region. This emission peak may be attributed to F-center oxygen vacancies [11]. In the 3% Cd doped MgO thin film, the peak is observed at 440 nm (2.82 eV) at the blue region. This emission peak may be ascribed to either the combination of the holes

from the valence band and the electrons from the conduction band or formed CdO in MgO [15]. The blue shift occurred with the Cd dopant, resulting in 382 nm (3.22 eV) at UV region. This shift may be resulted from the defect Cd such as substitutions, interstitial. The redshift occurred with the %1 and %2 Cd dopant, resulting in 540 nm (2.30 eV) at the green region. This peak may be attributed to either the aggregates of F_s centers or the defect Cd such as substitutions, interstitial [16]. This result similar the transmittance results. The emission intensity of 2.30 eV increases but the transmittance decreases rising Cd dopant in MgO. This peak may be related oxygen vacancy in structure similarly transmittance results beside of Cd defects [17]. When all the PL emissions are in the visible region, undoped and Cd doped MgO thin films can be used in optic display device applications.

3.5. XPS analysis

X-ray photoelectron spectroscopy (XPS) was also conducted to study the composition of the undoped and Cd doped MgO films. Fig. 6a compares the XPS survey spectra of the films. The wide-scan spectrum presented in Fig. 6a confirms the elemental signals from carbon (C), oxygen (O), magnesium (Mg) and cadmium (Cd) atoms in the sample. The C element is ascribed to absorbed carbon species. Fig. 6c shows the Mg 1s binding energy spectra for each sample. The high-resolution spectrum of Cd 3d is shown in Fig. 6d, which can be deconvoluted into two couple of peaks. Two obvious peaks located at 404.3 and 411.7 eV are observed, which are consistent with the values reported for Cd²⁺ [18, 19]. This result reveals that Cd element exists in the forms of Cd^{3d3/2} and Cd^{3d5/2} in the Cd doped MgO sample. Fig. 6b is the core level O 1s XPS spectrum. Only a distinct peak is observed at the binding energy of 532.1 eV, which is the characteristic value reported for O²⁻ [20]. The O 1s peak could be attributed to the adsorbed oxygen, while the O⁻ peak is apparently related to the lattice oxygen of MgO [21].

Conclusions

In this study, undoped and Cd doped MgO thin films were successfully grown and investigated by SILAR method on glass substrate. It has been demonstrated that PL results can be achieved with Cd dopant in the visible region, and it has been shown that these Cd doped MgO thin films can be used in optical display device applications.

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Figure captures

Fig. 1. X-ray diffraction patterns of undoped and Cd doped MgO thin films

Fig. 2. a) Absorbance, picture and b) transmittance of undoped and Cd doped MgO thin films

Fig. 3. Band gap variation of a) undoped MgO, b) 1% Cd, c) 2% Cd and d) 3% Cd doped MgO

Fig. 4. SEM images of a), b) undoped, c), d) 1%, e), f) 2%, g), h) 3% Cd doped MgO thin films

Fig. 5. PL spectra of undoped and Cd doped MgO thin films

Fig. 6. XPS spectra a) survey spectrum, b) O 1s, c) Mg 1s, d) Cd 3d of thin films

Table 1. hkl miller, 2θ , FWHM, d , intensity, D , a , V , E_g , Transmittance value of undoped and Cd doped MgO thin films

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Sample Name	<i>hkl</i>	Pos. ($^{\circ}2\theta$)	Height (cts)	FWHM ($^{\circ}2\theta$)	d -spacing ($\text{\AA}$)	I (%)	D (nm)	a ($\text{\AA}$)	V ($\text{\AA}^3$)	E_g (eV)	<i>Trans.</i> (%)
Undoped MgO	(200)	42.68	148.49	0.7871	2.120	100	23.13	4.2396	76.2045	4.36	35
	(220)	62.06	75.34	0.5914	1.496	51	26.43				
1% Cd	(200)	42.61	74.63	0.3936	2.122	100	47.55	4.2436	76.4183	4.17	18
	(220)	62.01	40.51	0.6888	1.497	54	22.93				
2% Cd	(200)	42.64	79.59	0.8856	2.120	100	20.88	4.2399	76.2207	4.24	24
	(220)	62.12	44.52	0.492	1.494	56	31.40				
3% Cd	(200)	42.76	244.65	0.1968	2.115	100	89.85	4.2302	75.6956	4.28	23
	(220)	62.09	129.41	0.5904	1.495	53	26.32				