Study of Ag Doping Effect on Structural and Electrical Properties of CdO Thin Films Prepared by SOL-GEL Technique with High Relatively Ag Concentrations (2.5%, 5% 10% and 15%) Prepared by Sol-Gel

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Abstract
Ag-CdO doped and pure CdO thin films prepared by sol-gel technique with spin coating method on glass substrates, Ag-CdO doped with relatively high concentration Ag (2.5%, 5% ,10% and 15%) as a try to obtain changes in structural and electrical properties of Ag-CdO doped thin films.

1. Introduction

Thin films have been extensively Studied for over last two hundred years because of their Potential uses[1], Transparent conducting oxide thin films such as zinc oxide (ZnO), indium tin oxide (ITO), tin oxide (SnO2) and cadmium oxide (CdO) are extensively used in semiconductor optoelectronic applications[2]. The physical properties like mechanical, electrical, magnetic and optical of thin films may differ from those of the bulk material are used commonly in the form of a deposit on a suitable substrate for integrated circuits like resistors, transistors and superconductors[3]. In recent years, researchers have focused on cadmium oxide (CdO) due to its applications, specifically in the field of optoelectronic devices such as solar cells[4]. The commonly used methods of preparation of semiconductor thin films are spray pyrolysis, sputtering, sol gel, vacuum evaporation , PLD, chemical bath deposition technique (CBDT), etc.[5].

2. Experimental

Thin films have been extensively studied for over last two decades because of their many applications[6], Transparent conducting oxide thin films such as zinc oxide (ZnO), indium tin oxide (ITO) and cadmium oxide (CdO) are extensively used in semiconductor optoelectronic applications[7]. The physical properties like mechanical, electrical, magnetic and optical of thin films may differ from those of the bulk material and are mainly used in deposition on preferred substrate for electronics parts and superconductors[8]. In recent years, many researchers focused on cadmium oxide (CdO) and CdO: dopants for its applications, specifically in the field of photovoltaic parts such as solar cells[9].

Pure Cadmium oxide show high transparence in the visible range of solar spectrum and show high electrical properties which represented low ohmic resistance[10 11].

According to Cadmium oxide (CdO) properties, is one of these important semiconductors oxides which has high optical properties. It has unique applications[12 13].

The commonly used methods of preparation of semiconductor thin films are sol gel method, spray

[1] K. L. Chopra, "Thin Film Phenomena", Mc Grow-Hill Inc., New York, 1969.
[2] Liu, X, Xu, Z, and Shen, Y, "A high performance ethanol gas sensor based on CdO-Fe2O3 semiconducting materials". Proc Int. Conf Solid State Sens. Act. 1, 585– 588, 1997.
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pyrolysis, evaporation, sputtering under vacuum, etc.[1], in recent study, Pure and Ag doped CdO thin films have been prepared by sol-gel spin coating method.

2. Experimental

Pure and Ag doped CdO thin films were deposited on glass substrates using sol–gel technique by spin coating method using VTC-200 (MTI CORP.) speed controlled spin coater. CdO solutions prepared from following materials:

1. (CAD) Cadmium acetate dehydrate $Cd(CH_3CO_2)_2$ (2g).
2. Methanol (14 mL).
3. Glycerol (100 µL).
4. Triethylamine (500 µL).

CdO precursor solution was firstly prepared as following procedure:

A. First solution: The cadmium acetate was dissolved in (7 mL) half of the methanol, for each g of (CAD) at constant magnetic stirring until obtaining a transparent solution, glycerol was added to the solution.
B. Second solution: the trimethylamine dissolved previously in the other half of the methanol (7 mL) was also incorporated. Storing the mixture of the two solution for 24 hours at RT.

The resulting solution is totally colorless and transparent in preparation and storing. The glass substrates were first treated by detergent, and then in methanol and acetone each for 10 min by using ultrasonic cleaner. At last, rinsing the substrates by de-ionized water and drying by nitrogen.

The dissolving of (0.85 g) silver nitrate in (50 ml) of methanol to prepare a silver and then doping the original solution with silver in three ratios of 2.5%, 5%, 10% and 15% of total solution volume. The coating solution was dropped into the glass substrate, which was rotated at 2000 rpm for (15 s) by spin coater. Films dried to 100^{o} c for one hour and annealed to 350^{o}c for 1 hour, using drying oven (EQ-DZF-6020-HT500P, MTI crop.), XRD diffraction spectra of the Pure and Ag doped CdO thin films was observed by ADX-2700 X-ray Diffraction Instrument (Angstrom advanced co ltd), The electrical parameters were observed by HMS-3000 (hall measurement system, ecopia co ltd).

3. Results and Discussions

3.1 structural properties of pure CdO and CdO:Ag doped thin films:

XRD pattern of Pure and Ag doped CdO thin films are shown in figures (figures 1-1, 1-2, 1-3, 1-4 and 1-5) to observe the changes in structural properties due to doping and ration of doping.

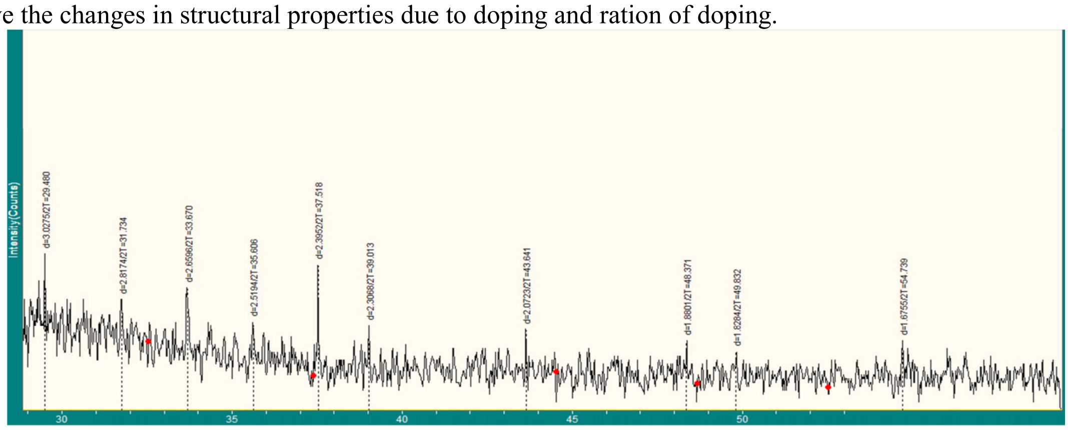

Figure (1-1) : XRD diffraction spectra for pure CdO.

[1] M.Ortega, G.Santana,and A.M.Acevedo, Superficies y Vaico, 9, 294- 295, 1999.

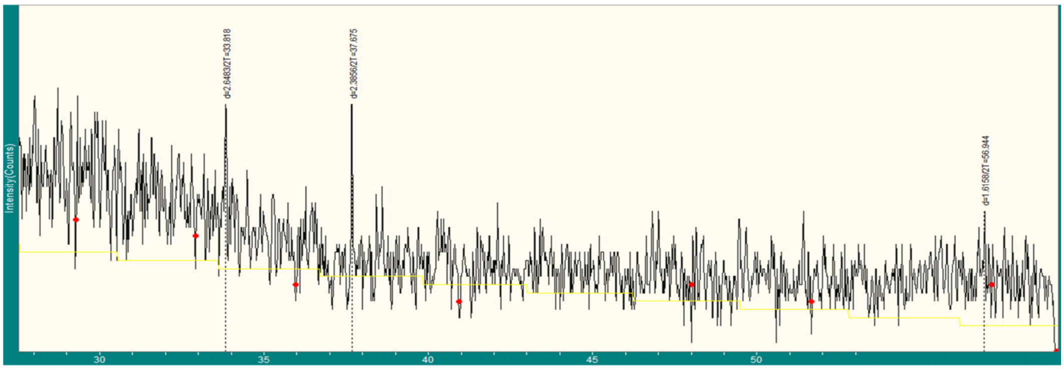

Figure (1-2) : XRD diffraction spectra for Ag doped CdO (2.5%).

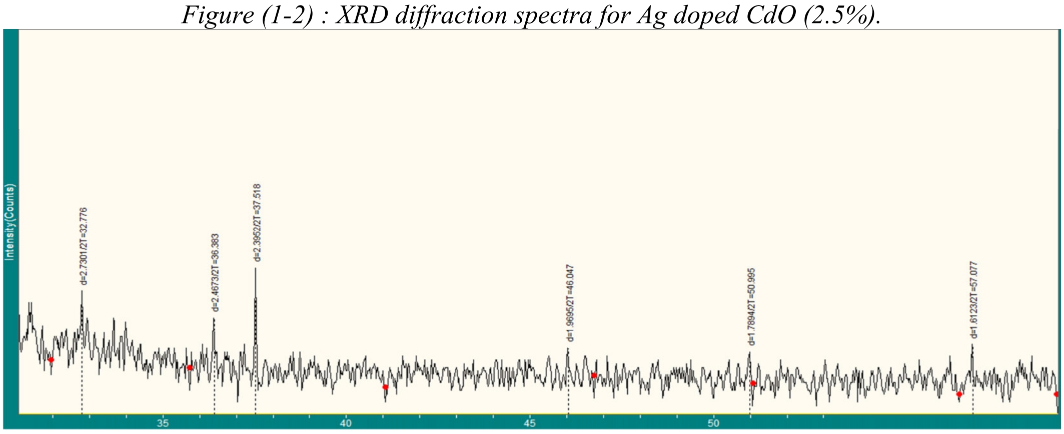

Figure (1-3) : XRD diffraction spectra for Ag doped CdO (5%).

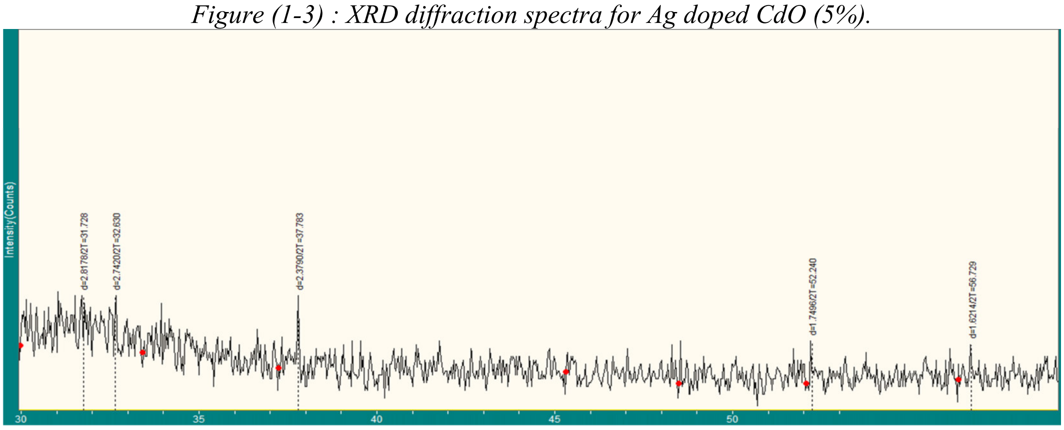

Figure (1-4) : XRD diffraction spectra for Ag doped CdO (10%).

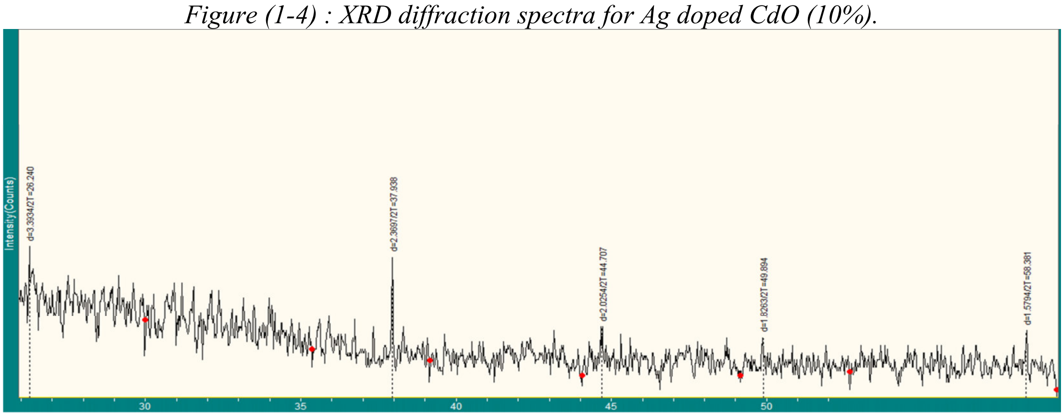

Figure (1-5) : XRD diffraction spectra for Ag doped CdO (15%).

XRD outcomes results demonstrate that the greater part of the Films have a polycrystalline structure. hkl Peaks (111), (200), and (220), for CdO thin films are in great concurrence with the reported information. The normal grain size for the films can be resolved by bragg equation[1] [1]:-

[1] J. S. Blakemore, "Solid State Physics", Cambridge University Press, 1985.

$$D = \frac{0.9 * \lambda}{\beta \cos\theta}$$

Where:
λ= wavelength.
β=FWHM (full width half maximum).
θ= the Bragg angle.
D =grain size

The planes (111), (200), and (220) indicate the CdO and CdO:Ag cubic rock salt phase with preferred orientation along the (111) planes. The observed diffraction patterns are in good agreement with the standard crystallographic data for the pure CdO of JCPDS card 05-0640. Since doping effect on structural specifications as we can observe, we should consider that increasing is in high ratios of Ag and increasing the doping ratio lead to unique change in crystallinity of films, in 2.5%CdO:Ag grain size D increase and this means that crystallization increasing is due to the particle size increased, for 5%CdO:Ag, 10%CdO:Ag and 15%CdO:Ag we observe decrease in grain size and this behaviour is due to fixed annealing temperature at 300◦c since The results of the doped sample show increasing in average grain sizes with increasing of temperature[2]. Doping CdO with Ag (with high concentrations doping ratios for5%CdO:Ag, 10%CdO:Ag and 15%CdO:Ag) should not lead to decrease grain size, it's slightly increasing along with (200) and (220) planes, we should notice that annealing temperature is fixed and increasing of annealing temperature should lead to increase grain growth for high doping concentrations, the details of the crystalline structure (interplanar distance dhkl and lattice constant a) of the films have been given in Table (1).

Table (1) : crystalline structure (interplanar distance dhkl and lattice constant a) of the pure CdO and CdO:Ag DOPED THIN FILMS.

SEQ.	SAMPLE ID	2-theta	Cos theta	d (measured)	d (standard)	muller factor			a	ß (FWHM)	D (grain size)
						h	k	l			
1	Pure Cdo	33.67	0.957142759	2.6596	2.68455	1	1	1	4.606562328	0.63	2.29940322
		37.518	0.946879626	2.3952	2.36809	2	0	0	4.7904	0.147	9.961398088
		54.739	0.888060235	1.6755	1.661	2	2	0	4.739029648	0.336	4.646764914
2	CdO:Ag (2.5%)	33.818	0.956767909	2.6483	2.68455	1	1	1	4.586990154	0.195	7.431751706
		37.675	0.946438135	2.3856	2.36809	2	0	0	4.7712	0.085	17.23539521
		56.944	0.879050191	1.6158	1.661	2	2	0	4.570172548	0.58	2.719510479
3	CdO:Ag (5%)	32.776	0.959373087	2.7301	2.68455	1	1	1	4.72867191	0.645	2.240707445
		37.518	0.946879626	2.3952	2.36809	2	0	0	4.7904	0.162	9.039046413
		57.077	0.878496287	1.6123	1.661	2	2	0	4.560273053	0.547	2.885394147
4	CdO:Ag (10%)	31.728	0.961913253	2.8178	2.68455	1	1	1	4.880572766	1.096	1.315182254
		37.783	0.946133403	2.379	2.36809	2	0	0	4.758	0.302	4.852584256
		56.729	0.879943097	1.6214	1.661	2	2	0	4.58601174	0.559	2.818811317
2	CdO:Ag (15%)	26.24	0.973896792	3.3934	2.68455	1	1	1	5.87754121	0.488	2.917424635
		37.938	0.945694587	2.3697	2.36809	2	0	0	4.7394	0.256	5.727189256
		58.381	0.873002955	1.5794	1.661	2	2	0	4.467217801	0.583	2.724257368

3.2 Electrical Properties of pure CdO and CdO:Ag doped thin films:

The electrical properties of the thin films have a great importance in determining the use of films in many applications especially in photovoltaic field. The electrical parameters could be determined by measuring the Hall Effect of the sample[3]. Measured data are listed in table -2-.

Table -2-:- electrical parameters observed by HMS-3000 hall measurement system for pure CdO and CdO:Ag doped thin films.

Items	resistivity rho (Ω*cm)	conductivity SIGMA (1/Ω*cm)	mobility µ (cm^2/Vs)	carrier concentration Nb (1 / cm^3)
Pure CdO	0.992	1.008	10.840	3.75E+17
(CdO:Ag) 2.5%	0.031	32.290	178.900	1.13E+18
(CdO:Ag) 5%	1722.000	0.001	52.450	6.91E+13
(CdO:Ag) 10%	1549.000	0.001	38.450	1.05E+14
(CdO:Ag) 15%	0.649	1.542	206.900	4.65E+16

One from The widely used techniques for obtaining hall reads for thin films is four-point probe (van der paw

[1] C. R. Brundle, C. A. Evans, J. S. Wihon And L. E. Fitzpatrick, "Encyclopedia of Mlaterials Characterization (Surfaces, Interfaces, Thin Films)", Butxetworch-Heinemann, A Division of Reed Publishing Cusa) Inc., 1992.

[2] M W Maswanganye, K. E. Rammutla, and B. W. Mwakikunga. The effect of silver (Ag) dopant on the structural and optical properties of sol gel prepared CdO nanoparticles, Department of Physics, University of Limpopo, P/Bag x1106, SOVENGA, 0727, South Africa Conference Paper, July 2014.

[3] Raman, PL And Hall Effect Studies Of Cdse Thin Film Deposited By Chemical Bath Deposition Bijumon C C, V.Senthil Kumar, INTERNATIONAL JOURNAL OF SCIENTIFIC & TECHNOLOGY RESEARCH VOLUME 5, ISSUE 05, ISSN 2277-8616, May 2016.

geometry at room temperature), The pure CdO and CdO:Ag films shape are square (2×2cm) and four InSn poles are maked by soldering regarding to HMS-3000 operating manual as shown in figure -2-, samples attached to The Spring Clip Board thin films holder (figure -3-) and being tested.

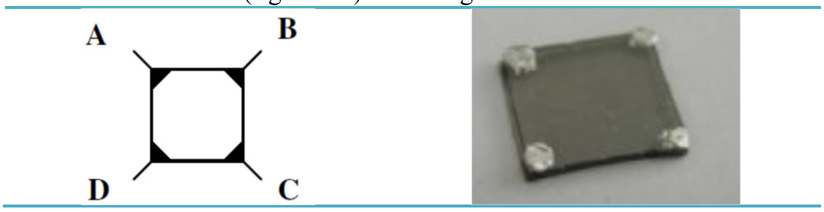

Figure -2-: poled thin films by soldering InSn .

Figure -3-: thin films holder for HMS-3000 hall measurement system.

Mobility dropped for 5% and 10% CdO:Ag concentrations (52.45 and 38.45 cm^2/Vs) from a high value of 2.5% CdO:Ag (178.9cm^2/Vs) which might be due to greater ionized impurity scattering[1 2].

Carrier concentration also dropped for 5%, 10% and 15% Ag concentration , the Ag-doping causes an increase in the carrier concentration in 2.5% CdO:Ag. the carrier concentration values dropped in alternatively higher doping values (+5%CdO:Ag doping ratios) and this can also be achieved by heavy doping. This decreasing might degrade the transparency and the mobility which cause more charge carrier scattering from the ionized impurities. Mobility and carrier concentration varying chart are shown in figure -4-.

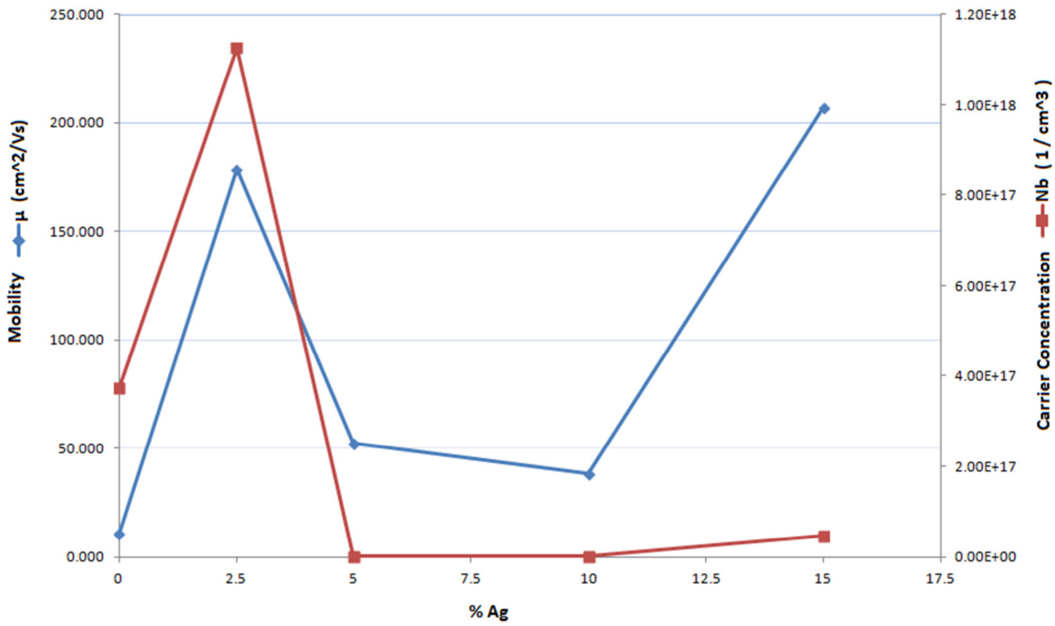

Figure -3-: mobility and carrier concentration variation VS CdO:Ag doping concentration

Conclusions

1. Coating by spin coating method (sol–gel technique) is suitable to obtain structural and electrical properties.
2. X-ray diffraction (XRD) preferred orientation for fixed annealing temperature of Ag:CdO high doping ratio is (111) plane.

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[1] Synthesis and characterization of aluminum-doped CdO thin films by sol–gel process, K.K. Chattopadhyay and Reevu Maity, Solar Energy Materials and Solar Cells 90(5):597-606, March 2006.

[2] Improved physical properties of spray pyrolysed Al:CdO nanocrystalline thin films, S. J. Helen, Suganthi Devadason, Journal of Materials Science Materials in Electronics, January 2016.

3. Due to high variation in electrical parameters, Ag doping in CdO films effectively increases the carrier concentration and mobility, in 2.5% doping ratio both mobility and carrier concentration increase due to uniformity of Ag substitutes in the lattice OF CdO as an effective n-type dopant rather than forming a second phase. and decreased in 5% and 10% due to greater ionized impurity scattering.
4. Hall Effect measurements show that Pure CdO film is n-type with an electron concentration of 3.75E+17 1/cm^3 and mobility of 10.840 cm^2 /Vs.

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