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Study Of Structural, Morphological And Optical Properties Of Pure CdO And Ag:CdO Doped Thin Films On Glass Substrates With High Relatively Ag Concentrations (2.5%, 5% 10% And 15%) Prepared By Sol-Gel Method

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Abstract: *Pure and Ag doped CdO thin films were 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%) to obtain changes in structural, Optical And Morphological properties of Ag:CdO doped thin films at fixed annealing temperature (300◦ C), the results Shows changes in structural properties at (111) plane due to fixed annealing temperature, and decreasing in direct energy gap, and show changes in roughness average.*

I. Introduction

Thin films have been extensively studied for over last two hundred years because of their Potential use[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 and are mainly used in deposition on preferred substrate for electronics parts and superconductors[3]. In recent years, researchers have focused on cadmium oxide (CdO) for its applications, specifically in the field of optoelectronic and photovoltaic parts such as solar cells[4].

Cadmium oxide (CdO) show high transparency in the visible region of solar spectrum and has high electrical properties which were represented low ohmic resistance[5] [6]. According to Cadmium oxide (CdO) properties, is one of these important semiconductors oxides which has high optical properties. It has unique applications[7] [8].

The commonly used methods of preparation of semiconductor thin films are sol gel, spray pyrolysis, sputtering, evaporation under vacuum, chemical bath deposition technique (CBDT), etc.[9], in recent study, Pure and Ag doped CdO thin films have been prepared by sol-gel spin coating method.

II. 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).

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[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).

[3] J. Thewlis, "Concise Dictionary of Physics and Related Subjects", 2nd edition, Pergamon Press, New York, (1979).

[4] K.Hame and S.E.San,"CdO/Cu2O solar cells by chemical deposition", Solar Energy, 77(3), 2004, 291-294.

[5] Structural, Morphological and Optical Properties of CDO: Al Thin Films Prepared by Chemical Spray Pyrolysis Methode Ramiz Ahmed Al-Ansari College of science for Women ,University of Baghdad , Jadriya, Baghdad, Iraq, IOSR Journal of Applied Physics (IOSR-JAP) e-ISSN: 2278-4861.Volume 8, Issue 1 Ver. II (Jan. - Feb. 2016), PP 06-15.

[6] TCO-Si Based Heterojunction Photovoltaic Devices Z.Q. Ma and B. He2, Shanghai P. R. China, ISBN 978-953-307-570-9, Publisher: InTech, Chapters published November 02, 2011 under CC BY 3.0 license, DOI: 10.5772/821.

[7] K. Siraj, PhD thesis, Institute of Applied Physics, Johannes Keple University Linz, Austria.2007.

[8] Optical and electrical properties of CU doped CdO thin films for detector applications G Salman, E Kareem, A. N. Naje, Physics department, college of science, University of Baghdad, Iraq. IJISET - International Journal of Innovative Science, Engineering & Technology, Vol. 1 Issue 6, August 2014, ISSN 2348 – 7968.

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

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 optical absorbance spectra of CdO and doped Ag:CdO thin films are recorded using double beam UV-VIS spectrophotometer (mega-2100, scinco co ltd) in the wavelength range 300 to 700 nm at room temperature, Morphological properties and surface shape pictures obtained by AA3000 scanning Probe Microscope by (angstrom advanced Inc.).

III. Results and Discussions

3.1 structural properties of Pure and Ag doped CdO 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.

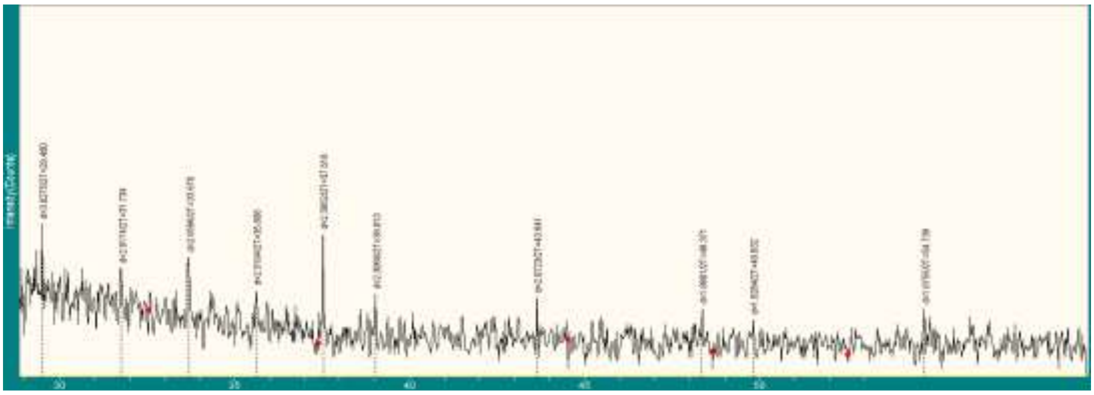


Figure (1-1): XRD diffraction spectra for pure CdO.

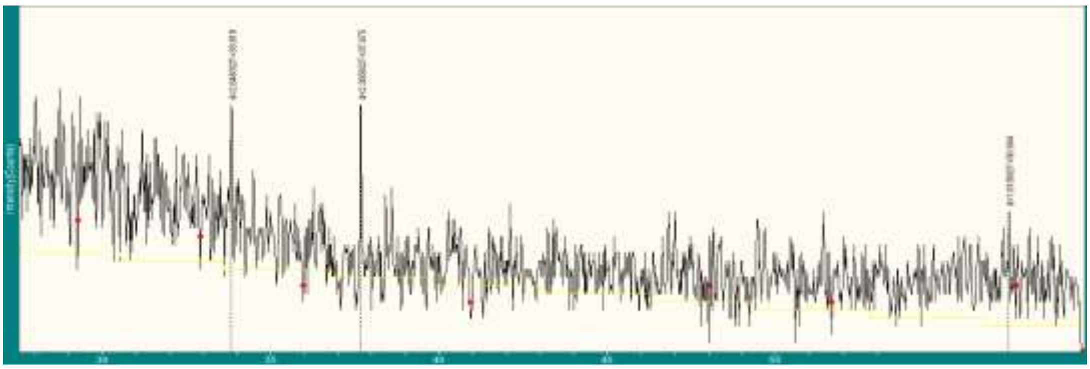


Figure (1-2): XRD diffraction spectra for Ag doped CdO (2.5%).

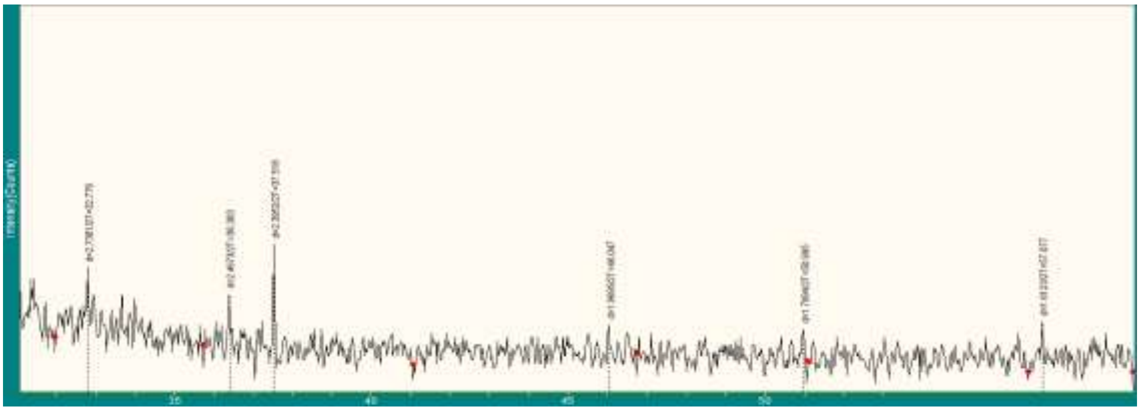


Figure (1-3) : XRD diffraction spectra for Ag doped CdO (5%).

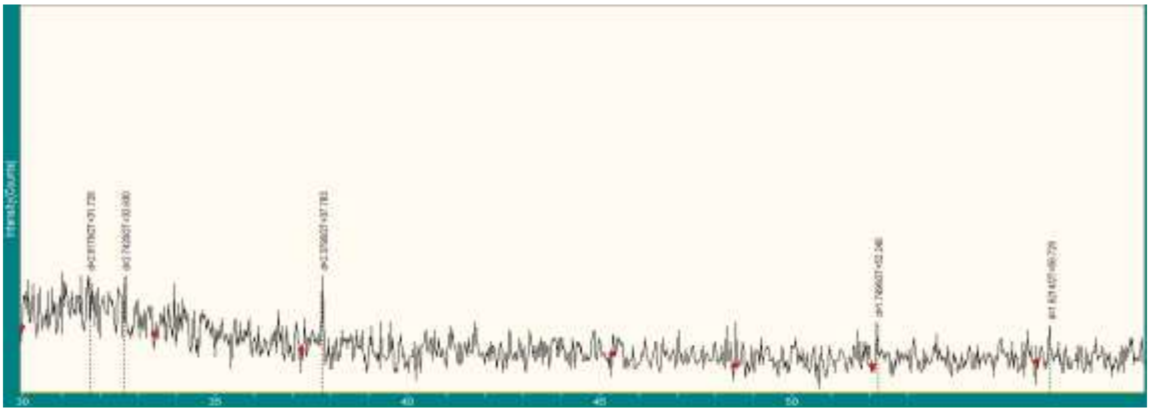


Figure (1-4): XRD diffraction spectra for Ag doped CdO (10%).

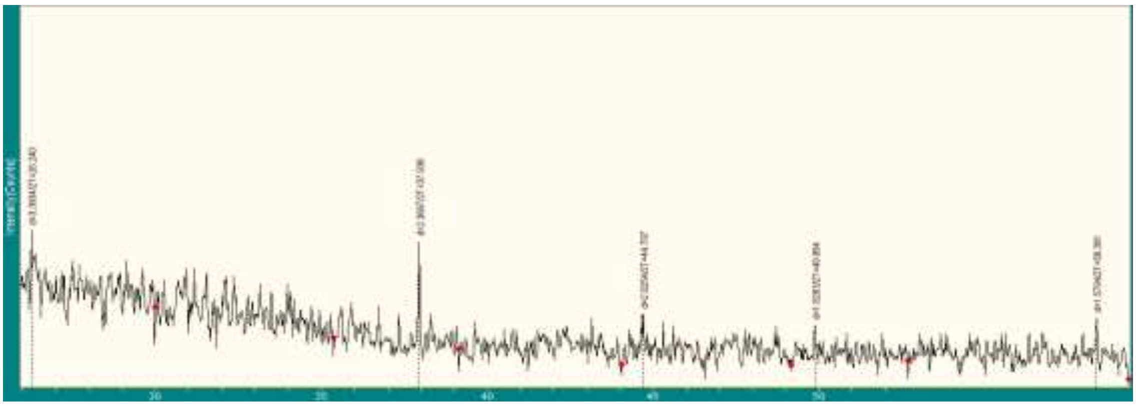


Figure (1-5): XRD diffraction spectra for Ag doped CdO (15%).

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[10 11]:-

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

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

[10] J. S. Blakemore, "Solid State Physics", Cambridge University Press, (1985).
[11] 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).

The planes (111), (200), and (220) indicate the CdO and Ag:CdO 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%Ag:CdO grain size D increase and this means that crystallization increasing is due to the particle size increased, for 5%Ag:CdO, 10%Ag:CdO and 15%Ag:CdO we observe decrease in grain size and this behavour 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[12]. Doping CdO with Ag (with high concentrations doping ratios for5%Ag:CdO, 10%Ag:CdO and 15%Ag:CdO) 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 Ag: CdO 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	Ag:CdO (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	Ag:CdO (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	Ag:CdO (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	Ag:CdO (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 Optical properties of Pure and Ag doped CdO thin films:

The optical absorbance spectra of CdO and doped Ag:CdO thin films are recorded using double beam UV-VIS spectrophotometer (mega-2100, scinco co ltd) in the wavelength range 300 to 700 nm at room temperature. Absorbance spectra are shown in figure -2-, From the figure, we can observe absorption excitonic peaks at ~400 nm for undoped CdO and ~430 nm for the 2.5% Ag doped CdO samples annealed to 300◦ C, for the 2.5%Ag:CdO, we can observe unique increasing in absorbance spectra from 700 nm to 480 nm and increasing in absorbance spectra from 480 nm to 330nm, this behavior is not same for 5%Ag:CdO, 10%Ag:CdO and 15%Ag:CdO, Since we can observe clear increasing in absorbance spectra for these high doping ratios. The energy gap values are depended in general on the films crystal structure. The arrangement and distribution of atoms in the crystal lattice also are affected by crystal regularity. The optical energy gap values (Eg) of CdO thin films have been determined by using Tauc relation[13]:

$$\alpha(h\nu) = A\left(h\nu - E_g^{opt}\right)^r$$

Where:
A: is a constant.
Hυ: is the photon energy.
Eg: is the optical band gap.
r: is constant which takes the values (1/2, 3/2, 2, 3) depending on the material and the type of the optical transition.
Energy gap estimated by plotting the $(\alpha h\upsilon)^2$ versus photon energy (hυ), the determination of (Eg) is made by extrapolating the linear portion of the curves until they intercept the photon energy axis, as shown in fig. -3-, from the figure we can observe slightly decreasing in Direct energy gap for the 2.5% Ag:CdO from the pure

[12] 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
[13] J. Tauc, "Amorphous and Liquid Semiconductors", Plenum Press, USA, (1974).

CdO thin films. wide decreasing for 5%Ag:CdO, 10%Ag:CdO and 15%Ag:CdO as shown in table -2-. Absorbance spectra and direct energy band behavior nearly matched with many published results[14 15 16].

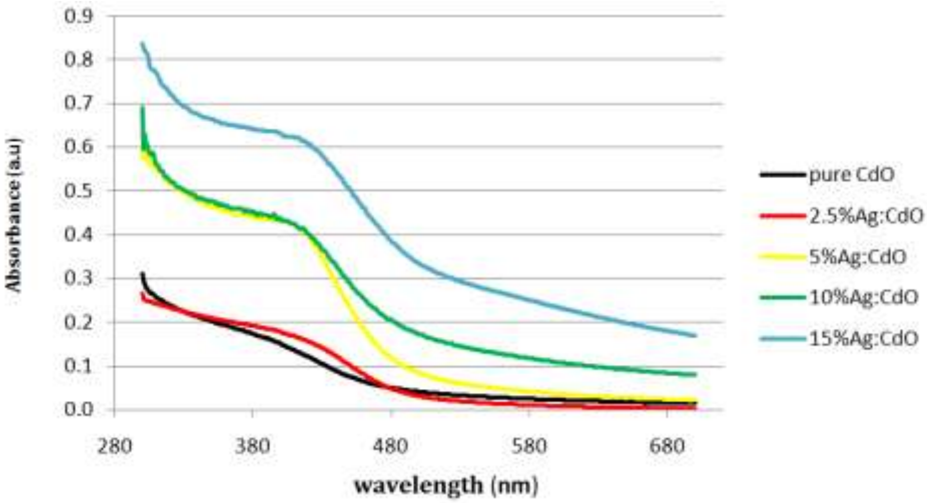


Figure -2- : Absorbance spectra for Pure CdO and doped Ag:CdO THIN FILMS

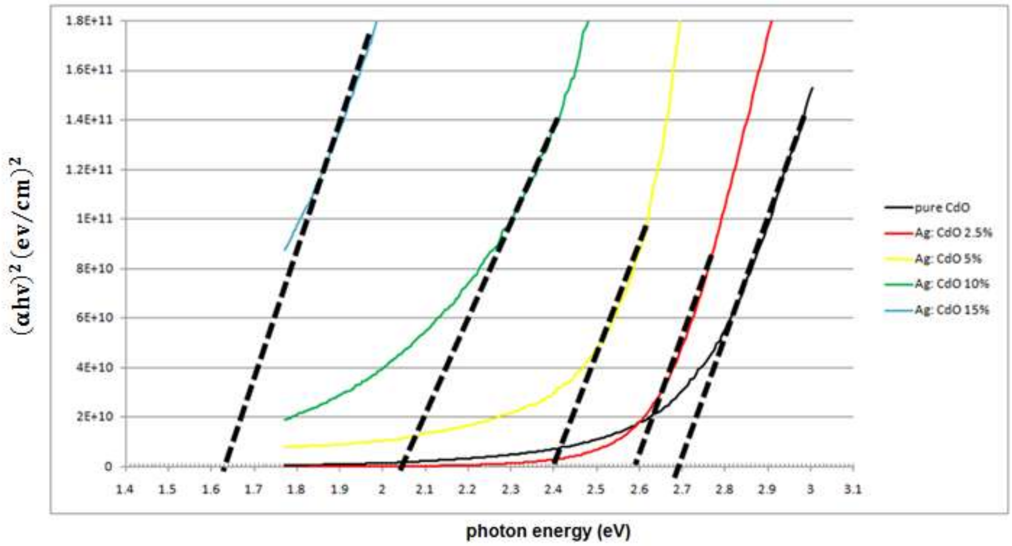


Figure -3- : Direct energy gap spectra for Pure CdO and doped Ag:CdO THIN FILMS

Table (2): The Values Of The Direct Energy Gap Of Pure Cdo And Ag:Cdo Doped Thin Films.

Items	**Eg 300 ºC (eV)**
Pure CdO	2.69
2.5%Ag:CdO	2.59
5%Ag:CdO	2.4
10%Ag:CdO	2.05
15%Ag:CdO	1.64

[14] Some Optical Properties of CdO Thin Films, Ghazi Y. Naser, gazy2005@yahoo.com, Waleed N. Raja, Ali S. Faris, Zenhe J. Rahem, Mohammed A. Salih, Auday H. Ahmed, Al-Iraqia University, College of Education, Physics department; Baghadad, Iraq, 2013.

[15] Characterization of CdO Thin Films Prepared By SILAR Deposition Technique, M.Mahaboob Beevia , M.Anusuyab, V.Saravananc* IACSIT Member, International Journal of Chemical Engineering and Applications, Vol. 1, No. 2, August 2010, ISSN: 2010-0221

[16] Properties of CdO Thin Films Produced by Chemical Vapor Deposition, X. Li, D. L. Young, H. Moutinho, Y. Yan, C. Narayanswamy, T. A. Gessert and T. J. Couttsz, Electrochem. Solid-State Lett. 2001 volume 4, issue 6, C43-C46.

Decreasing of energy band gab is due to increasing of impurities that create new phases inside band gap over the equivalent edge and under conductive edge, it's also increase density of this phases by increasing doping ratio by Ag and this doping lead to minimize band gap respectively into lowest energy band gap at 15% Ag:CdO ratio.

3.3 Morphological properties:

The results of SPM are matched with the XRD results as the grain size and diameter increases with Ag doping ratio with respect to fixed annealing temperature and crystallinity improves for the whole 2.5%Ag:CdO, 5%Ag:CdO, 10%Ag:CdO and 15%Ag:CdO thin films stay as indicated by the broadening of the XRD peaks. Figure -4- show AFM image for pure CdO thin film.

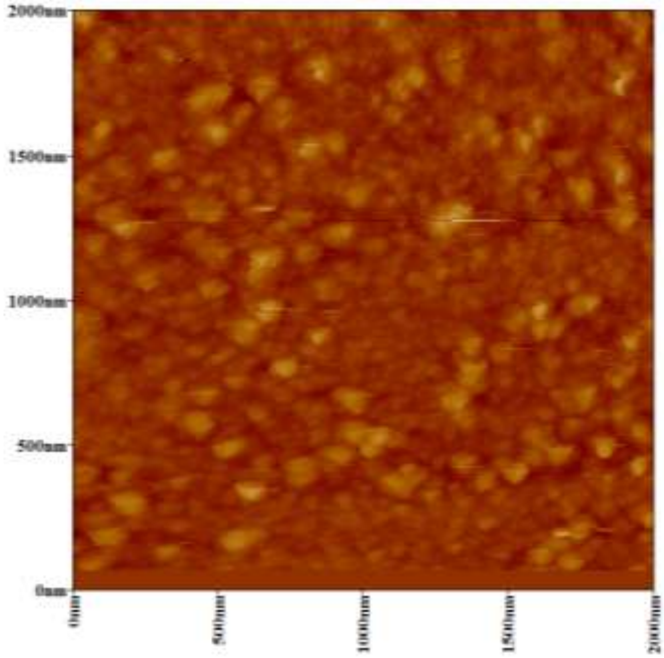


Figure -4- : SPM images of CdO pure thin film.

Samples clearly show that films are uniform and polycrystalline, as well as void-free. The (Sa) root mean square roughness and the average grain size are shown in table (3), results show increasing in Sa for 2.5% and 5% Ag doping ratio and decrease for 10% and 15% Ag doping ratio and images show closely uniform spherical shape grains, results match previous publications [17] [18].

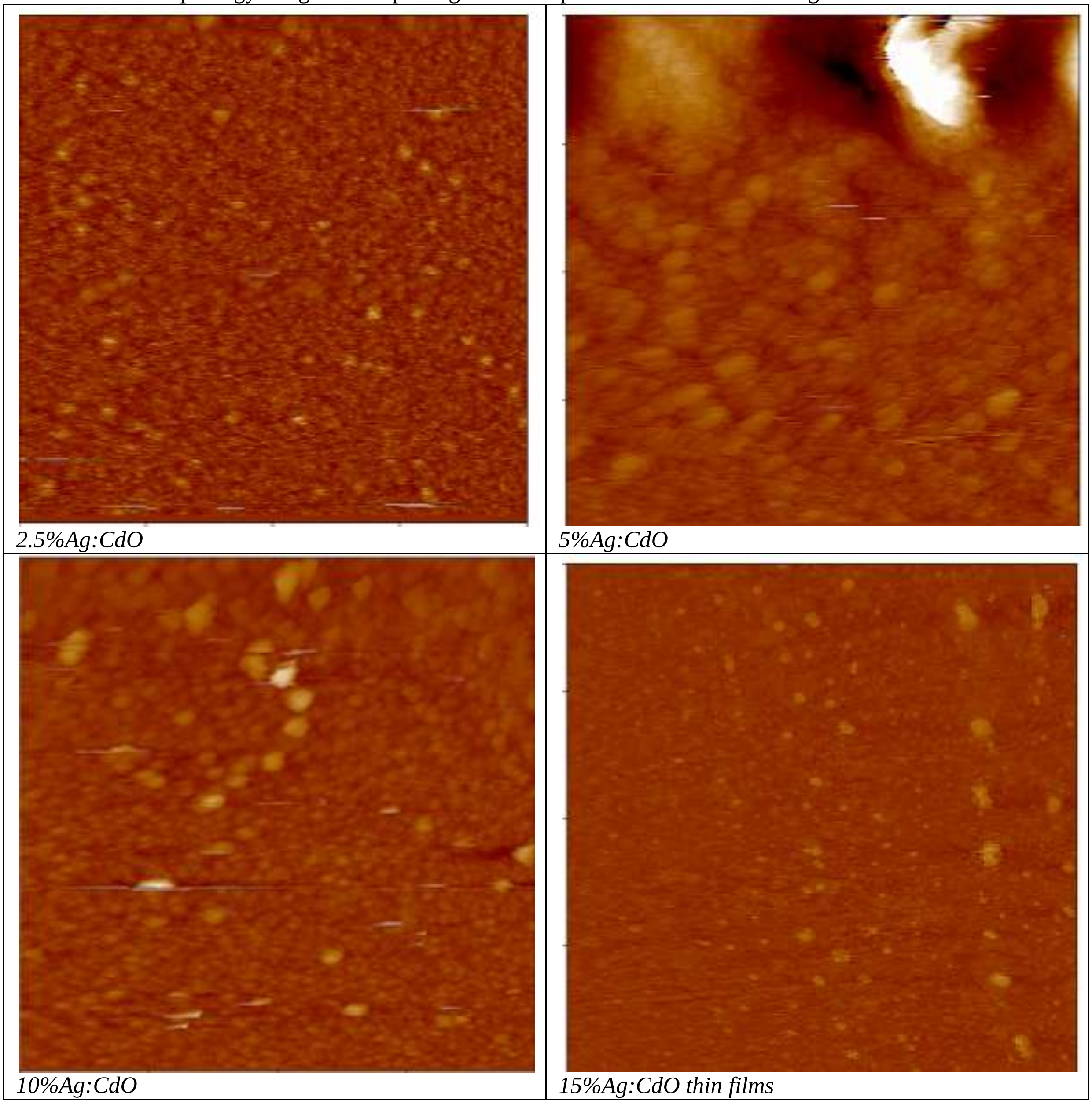
Table -3- : average grain diameter, average grain size and roughness average for pure CdO and doped CdO:Ag samples

sample	AVG size grain diameter (nm)	AVG size grain size (nm)2	Sa Roughness average (nm)
Pure CdO	24.11	456	1.37
2.5 % Ag:CdO	21.35	358	2.97
5 % Ag:CdO	32.48	828.7	2.25
10 % Ag:CdO	25.5	514	1.23
15 % Ag:CdO	17.9	253	0.923

[17] High transmittance CdO thin films obtained by the sol-gel method, D.M. Carballeda-Galicia, R. Castanedo-P´erez, O. Jim´enez-SandovalU, S. Jim´enez-Sandoval, G. Torres-Delgado, C.I. Z´u˜niga-Romero, Thin Solid Films 371 2000. Pages 105-108.

[18] Temperature dependence growth of CdO thin film prepared by spray pyrolysis, Hassan H. Afify, Ninet M. Ahmed, Magdy, Y. Tadros, Fatma M. Ibrahim, Journal of Electrical Systems and Information Technology, Volume 1, Issue 2, September 2014, Pages 119–128.

SPM surface morphology images for doped Ag: CdO samples are shown in below figures:



2.5%Ag:CdO *5%Ag:CdO*

10%Ag:CdO *15%Ag:CdO thin films*

Figure -5- : SPM images of doped 2.5%Ag:CdO, 5%Ag:CdO, 10%Ag:CdO and 15%Ag:CdO thin films.

IV. Conclusions

The Pure CdO and doped 2.5%Ag:CdO, 5%Ag:CdO, 10%Ag:CdO and 15%Ag:CdO thin films were deposited by sol–gel method spin coating technique. The structural and optical properties of the CdO film were obtained, we can observe following points:

1. Coating by sol–gel technique spin coating method is suitable to obtain structural and optical properties.
2. X-ray diffraction (XRD) preferred orientation for fixed annealing temperature of Ag:CdO high doping ratio is (111) plane.
3. Ag high doping concentration affects the optical parameters of the thin films, it leads to reduction of direct energy gap Pure CdO 2.69, 2.5%Ag:CdO 2.59, 5%Ag:CdO 2.4, 10%Ag:CdO 2.05, 15%Ag:CdO 1.64.

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