Highly Conducting Cr-doped CdO Films Annealed in Different Atmospheres for Optoelectronic Applications

A. A. Dakhel and W. E. Alnaser

Department of Physics, College of Science, University of Bahrain, P.O. Box 32038, Kingdom of Bahrain

Abstract: A set of CdO doped with 1.5% chromium thin films have been grown on glass substrates. The prepared films were annealed in H2, N2, and NH3 atmospheres. The structural, electrical, and optical properties of the annealed films were systematically studied. The structural investigations demonstrate that the included Cr ions dissolved in CdO lattice. It was concluded that Cr3+ ions most likely occupied interstitial locations of CdO lattice and behave as donors. Annealing in different atmospheres has considerable effects on the films crystallinity and orientation so that the films becam highly [111] oriented with annealing in NH3 gas. An improvement of all electrical conduction parameters by Cr doping and more improvement of conductivity and carrier concentration by annealing in H2, N2, or NH3 atmospheres was observed. Bandgap widening observed with annealing was explained and theoretically calculated.

Introduction

CdO is one of transparent conduction oxides (TCO) such as ZnO, SnO$_2$, Ga$_2$O$_3$, In$_2$O$_3$, etc. This group of oxides have widespread manifold applications in optoelectronic technology. It is used in the field of flat panel displays, solar energy systems, etc [1-5]. Furthermore, for the diversity of applications, some additional properties need to be introduced in TCO, like ferromagnetic, hardness, etc. Such hybridization of properties was materialized by doping of TCO with certain ions having that property that required to be appeared in the host TCO. Thus, the object of doping of TCOs is to improve their ordinary functions in addition to create an additional extra property that normally does not exist in that host TCO.

CdO is an n-type semiconductor with a direct bandgap of 2.2 - 2.7 eV [1,6,7]. It has high conductivity (10^2 – 10^4 S/cm) and transparent properties in visible and NIR spectral regions. In general, the Opto-electrical properties of doped CdO films depend on their internal microstructure, which is controlled by the preparation conditions. The electrical properties of doped CdO films are controlled by the scattering of carriers by impurities and defects including the grain boundaries (GBs) and crystallite boundaries (CBs).

On the other hand, chromium can improve the corrosion resistance and hardness when adding to some materials [8-10]. Thus doping of host CdO with Cr ions would create some useful mechanical properties. The present fundamental work reports the structural, electrical, and optical properties of Cr-doped CdO films annealed in different atmospheres: H$_2$, N$_2$, and NH$_3$ gas.

The Shannon ionic radius of Cd^{2+} is 0.095 nm for coordination number CN=6 and it is 0.0615 nm for Cr^{3+} ions [11]. Thus Cr^{3+} ions can enter into the crystalline structure of host CdO and improve it's conduction parameters, especially the carrier mobility similar to B- and W-doped CdO [12,13]. It must be mentioned that doping of TCO with Cr^{3+} was performed for ZnO [14-16], SnO$_2$ [17], and In$_2$O$_3$ [18,19].

2. Experimental details

A series of Cr-doped CdO thin films were deposited on ultrasonically cleaned glass slides held in a vacuum chamber of residual oxygen atmosphere ~ 1.3×10^{-3} Pa.

E-mail: akildakhil@gmail.com, alnaserw@gmail.com

The starting materials, pure Cr and CdO (from Fisher sci. company/USA and Fluka A.G./Germany, respectively) were evaporated alternatively (layer by layer…) by alumina baskets (Midwest tungsten service, USA). The evaporated masses were controlled with a piezoelectric microbalance crystal sensor (Philips FTM5) fixed close to the substrate. The as-grown films were totally oxidised by flash annealing in air at 400 ^{o}C for 1 h keeping samples inside the closed furnace for slow natural cooling to room temperature. The samples were annealed in different atmospheres: H_2, N_2, and NH_3 gas. All these 3-kinds of annealing were done at 300 ^{o}C for 30 min. The measurements and characterisations were carried out after annealing. The films thickness was measured by an MP100-M spectrometer (Mission Peak Optics Inc., USA) to be about 0.19 μm. The energy dispersive X-ray fluorescence (EDX) method was used to determine the relative mass-content ratio Cr to Cd in the prepared films on Si substrates. The mass ratio was determined with the well-known micro radiographic analysis method [20] by measuring the ratio of the fluorescent intensities of Cd L-signal at 3.13 keV and Cr K_α-signal at 5.41 keV in the sample and in the references. The reference samples were known pure Cr and CdO thin films. The crystalline structure was determined by the X-ray diffraction (XRD) method with a Philips PW 1710 θ -2θ system with a Cu K_α radiation. The spectral optical transmittance T(λ) in UV-VIS-NIR spectral region (300 – 3000 nm) was measured at normal incidence with a Shimadzu UV-3600 double beam spectrophotometer. The electrical measurements were carried out with a standard Van-der-Pauw method a magnetic field of about one Tesla and using a Keithley 195A digital multimeter and a Keithley 225 current source

3. Results and discussion

3.1. Structural characterisation

Fig.1 shows the XRD patterns of the prepared CdO:Cr films with that of CdO and Cr_2O_3 films grown on glass substrates for comparison. The patterns reveal that all the investigated films are polycrystalline of cubic (Fm3m) structure. The calculated lattice parameter of CdO:Cr film is about 0.4686 nm, which is slightly less than 0.4694 nm found for CdO film (The JCPDS [21] value of powder CdO is 0.4695 nm). This difference can be attributed to the effect of small size of Cr^{3+} ions doped in CdO lattice. Furthermore, any peak corresponding to Cr or Cr-oxide was not found as shown in fig.1. The prepared Cr-oxide thin film crystallized at 400 ^{o}C into Cr_2O_3 phase of trigonal

structure of a=b=0.4953 nm and c=1.3578 nm [22]. This implies that Cr ions were dissolved in the lattice of CdO.

However, the probability of formation of substitutional solid solution (SSS) by replacement of Cd^{2+} ions with Cr^{3+} ions is small since such substitution if it happened would strongly deform the cubic structure of CdO as the % difference of ionic radii is large ~ 35%. Therefore, the majority of Cr^{3+} ions could occupy interstitial positions in CdO lattice (Cr_i). Such incorporation of Cr^{3+} ions disturbs the charge balance that can be settled by creation of Cd^{2+}-ion vacancies (V_{Cd}). Some of the Cr^{3+} ions that occupy interstitial positions might move by thermal motion to occupy Cd^{2+}-ion vacancies (V_{Cd}). However, the formation of V_{Cd} reduces the unit-cell volume [23].

It was established that the present annealing in different gases has no appreciable effect on the lattice parameters. Furthermore, the annealing in H_2 or N_2 atmosphere has no appreciable effect on the preferred orientation of CdO film. Only the annealing in NH_3 gas has clear effect on the preferred orientation of the film so that it becomes highly [111] oriented, as shown in fig.1. Thus, the intensity ratio ($I_{(200)}/I_{(111)}$) was ~ 40% in CdO:Cr film became ~ 5% when it was annealed in NH_3 gas.

The results show that annealing in H_2, N_2, or NH_3 gas can help Cr ions to incorporate in CdO lattice as well as affects the CBs and GBs (this point will be discussed in the next section).

The present-work films grown on glass substrates have the usual, energy preferred [111] orientation. The mean X-ray crystallite size (CS) can be estimated from the most intensive (111) reflection by using Scherrer equation [24]: CS= 0.9λ/βcosθ, where λ is the X-ray wavelength; β is the full-width at half maximum (FWHM) of the diffraction peak (in radian); and θ corresponds to the Bragg peak position. The nano-CS (~30-35 nm) for CdO:1.5%Cr doped CdO film annealed in different gases, which means that the annealing in different gases has no considerable effect on crystallite size.

3.2. Electrical properties

The standard Van-der-Pauw method was used to measure the electrical conduction parameters (ECPs) [conductivity (σ), mobility (μ_{el}), and carrier concentration (N_{el})] and the average results are presented in table 1. The first observation is that all the investigated samples have n-type degenerate semiconducting properties. All the ECPs were

enhanced with Cr doping. However, under annealing N_{el} and σ were improved meanwhile μ_{el} decreased. This means that all types of annealing have their influence through reducing the potential barriers or depletion regions formed on grain boundaries leading to reduction in resistivity and increasing the effective number of carriers participate in dc-conduction [25]. The accumulation of gas atoms on CBs and GBs deteriorated the crystalline quality of the film that enhanced the scattering of free carriers and reduced μ_{el}.

The carrier concentration of CdO (4.4×10^{19} cm^{-3}) was strongly increased up to 1.2×10^{20} cm^{-3} with 1.5% Cr doping. This indicates that almost the majority incorporated Cr ions act as donors. Table.1 shows that annealing in H$_2$, N$_2$, or NH$_3$ further increased the carrier concentration.

Doping with Cr ions enhances the mobility of the carriers by about 9.5 times indicating that such doping creates spatial allowable routes inside the CdO crystalline structure leading to increase the carrier mobility in spite of increasing their concentration. However, decreasing of mobility of carriers in Cr-doped CdO due to the annealing in different atmospheres is related to the deterioration of crystalline structure and increasing in carrier concentration. Therefore, the inverse relationship between conduction carrier concentration and their mobility of Cr-doped CdO samples annealed in different gases N$_2$, H$_2$, and NH$_3$ was observed, as shown in fig.2. It is important to mention that P-type ZnO films were obtained with annealing in NH3 gas [26,27]. However, for CdO:Cr films, annealing in NH3 gas at 400 $^{\circ}$C and 500 $^{\circ}$C produced usual n-type conduction. However, when the annealing temperature was raised to 600°C, the films dissociated forming amorphous Cd film, and the films disappeared with the 700 $^{\circ}$C-annealing.

3.3. Optoelectronic properties

The normal transmittance T(λ) for all films prepared on corning glass substrates in UV-VIS-NIR region (300–3000 nm) are depicted in fig.3. The T(λ) spectra have their maxima in the NIR region, where showing a clear damping due to the high density of free electrons. The absorbance $A(\lambda)$ can be calculated from the experimental data by $A(\lambda) = \ln(1/T)$ [28]. The inset of fig.2 shows the graphical relationship of absorption coefficient, α vs. N_{el} (α=A/d, where d is the film's thickness). It shows that α increases with N_{el} until about 2.49×10^{20} cm^{-3}, then decreases. It means that the experimentally measured α at NIR spectrum range depends not only on the free electron density but also on the film's structural defect density that scatters the light.

The optical band gap E_g is evaluated according to the well-known relation [29]:

$$(A E)^m = B_{op} (E - E_g) \qquad (1)$$

where B_{op} is the film's constant and the exponent m is equal to 2 or 0.5 for direct or indirect transitions, respectively. Thus, the extrapolation of the Tauc plot, $(AE)^2$ vs. E for any sample, as shown in fig.4, gives the values of it's direct band gap (table 1).

For undoped CdO film, the bandgap obtained was in the range (2.2 eV- 2.6 eV) that is known for CdO films prepared by different techniques [1]. It is clear that the bandgap varies with variation of carrier concentration. Indeed, there are two competing phenomena simultaneously control E_g. These are the bandgap widening (BGW) and bandgap narrowing (BGN). The BGW is described by Moss-Burstein (BM) band-filling model, in which the band-edge energy is blue-shifted with increasing carrier concentration according to [30,31]: $\Delta E_g^{BGW} = S_{BGW} N_{el}^{2/3}$, where $S_{BGW}^{th} = 1.348 \times 10^{-18}$ eV.m^2 [30,32]. The BGN arises from electron-impurity and electron-electron interaction is given by: $\Delta E_g^{BGN} = -(S_{BGN}^{(1)} N_{el}^{2/3} + S_{BGN}^{(2)} N_{el}^{1/3})$, where $S_{BGN}^{(1)} = (1/3)S_{BGW}^{th}$ eV.m^2, $S_{BGN}^{(2)} = 2.836 \times 10^{-9} / \varepsilon_r$ eV.m, and for the dielectric constant ε_r it is possible to use ε_∞ ($\varepsilon_\infty = n^2 = 1.6^2$) [32-34]. Thus, the overall bandgap shift is $\Delta E_g = \Delta E_g^{BGW} + \Delta E_g^{BGN} = S_{BGW,BGN} N_{el}^{2/3} - S_{BGN}^{(2)} N_{el}^{1/3} + C_f$, where C_f is some fitting parameter and $S_{BGW,BGN} = S_{BGW} - S_{BGN}^{(1)} = 8.98 x 10^{-19} eV .m^2$. Accordingly, a straight-line relation between OEF vs. $N_{el}^{1/3}$ should be obtained, where the optoelectronic function $OEF = E_g - S_{BGW,BGN} N_{el}^{2/3}$. Actually, a straight line was obtained, as shown in the inset of fig.4. The fitting gave $S_{BGN}^{(2)} = 3.80 \times 10^{-9}$ eV.m, which has the same order on magnitude as the theoretical value $S_{BGN}^{(2)} (th) = 1.107 \times 10^{-9}$ eV.m; the difference might come from the non-parabolic band effects and micro morphology structure including GBs that was not entered in the correlation.

4. Conclusions

The structural investigation shows that the incorporated Cr ions dissolved in CdO lattice. It was concluded that Cr^{3+} ions most likely occupied interstitial locations of CdO lattice. The entered Cr^{3+} ions in CdO lattice behave as donors. It was observed that annealing of 1.5%Cr-doped CdO in different atmospheres H2, N2, and NH3 have a negligible effect on the lattice parameters. The annealing has effect on crystallinity and film orientation so that it becomes highly [111] oriented with annealing in NH3 gas. With 1.5%Cr doping of CdO, all ECPs were improved: conductivity by 25.8 times, mobility by 9.5 times, and carrier concentration by 2.7 times. Further improvement of conductivity and carrier concentration with annealing in H2, N2, or NH3 atmospheres was observed. In conclusion, chromium is sufficiently effective dopant for applications in infrared transparent-conducting-oxide (IR-TCO) applications.

Table 1. The measured resistivity ρ ($\times 10^{-4}$ Ω.cm), carrier concentration N_{el} (10^{20} cm^{-3}), mobility μ_{el} ($cm^2/V.s$), and bandgap E_g *(eV)* for Cr-doped CdO films grown on glass substrate.

Sample	ρ	N_{el}	μ_{el}	E_g
CdO	201	0.44	7.1	2.26
CdO:1.5%Cr-ann. air	7.78	1.25	66.78	2.4
CdO:1.5%Cr-ann. H_2	4.68	2.49	53.4	2.1
CdO:1.5%Cr-ann. NH_3	5.58	2.06	54.4	2.06
CdO:1.5%Cr-ann. N_2	4.48	2.86	48.7	1.95

References

[1] Z. Zhao, D. L. Morel, C. S. Ferekides, Thin Solid Films 413 (2002) 203.

[2] Y. Dou, R. G. Egdell, T. Walker, D. S. L. Law, G. Beamson, Surface Science 398 (1998) 241.

[3] A. A. Dakhel, Phys. Stat. Sol. (a) 205 (2008) 2704.

[4] R. K. Gupta, K. Ghosh, R. Patel, S. R. Mishra, P. K. Kahol, Curr. Appl. Phys. 9 (2009) 673.

[5] A. A. Dakhel, Thin Solid Films 518 (2010) 1712.

[6] D. M. Carballeda-Galicia, R. Castanedo-Perez, O. Jimenez-Sandoval, S. Jimenez-Sandoval, G. Torres-Delgado, C. I. Zuniga-Romero,Thin Solid Films 371 (2000) 105.

[7] M. Burbano, D. O. Scanlon, G. W. Watson, J. Am. Chem. Soc. 133 (2011) 15065.

[8] R. N. Thangaraj, M. R. Munteanu, E. Girt, M. J. Stirniman, T. P. Nolan, USA patent US007,998,606B2, Aug. 16, 2011

[9] F. Pearlstein, V. S. Agarwala, U.S. Patent No. 5374347, 20 Dec. 1994

[10] J. Jagielski , A. S. Khanna, J. Kucinski, D. S. Mishra, P. Racolta, P. Sioshansi, E. Tobin, J. Thereska, V. Uglov, T. Vilaithong, J. Viviente, Si-Ze Yang, Anton Zalar, Applied Surface Science 156 (2000) 47.

[11] R. D. Shannon, Acta Crystallographica A 32 (1976) 751.

[12] A. A. Dakhel, J. Mat. Sci. 46 (2011) 6925.

[13] A. A. Dakhel, J. Electronic materials 41 (2012) 2405.

[14] L. Li, H. Liu, X. Luo, X. Zhang, W. Wang, Y. Cheng, Q. Song, Solid State Communications 146 (2008) 420

[15] K. Sato, H. Katayama-Yoshida, *Semicond. Sci. Technol.* 17 (2002) 367.

[16] R. S. Ajimsha, A. K. Das, B. N. Singh, P. Misra, L. M. Kukreja, Physica B 406 (2011) 4578.

[17] S. –J. Liua, L. –Y. Chen, C. –Y. Liu, H. –W. Fang, J. –H. Hsieh, J. –Y. Juang, Appl. Surf. Sci. 257 (2011) 2254.

[18] D. N. Chavan, G. E. Patil, D. D. Kajale, V. B. Gaikwad, G. H. Jain, **Sensors & Transducers J.** 125 (2011)142.

[19] L. San-Bing, L. Jun-Qian, Chinese J. Struct. Chem. 28 (2009) 360.

[20] J. M. Jaklevic, F. S. Goulding, "Energy Dispersion" in "X-ray Spectrometry" H. K. Herglotz, L. S.Birks (eds.), P.50, NY: M. Dekker, 1978.

[21] Powder Diffraction File, Joint Committee for Powder Diffraction Studies (JCPDS) file No. 05- 0640.

[22] Powder Diffraction File, Joint Committee for Powder Diffraction Studies (JCPDS) file No. 38-1479.

[23] A. A. Dakhil, H. Hamad, Int. J. Thin. Films Sci Tech. 1 (2012) 25.

[24] J. I. Langford, A. J. C. Wilson, J. Appl. Cryst. 11(1978) 102.

[25] A. A. Dakhel, Semicond. Sci. Technol. 23 (2008) 055017 (6pp).

[26] E. S. Jung, H. S. Kim, H. K. Cho, J. H. Kim, Superlattices and Microstructures 42 (2007) 62.

[27] L. –D. Tang, Y. Zhang, X. –Q. Yan, Y. –S. Gu, Z. Qin, Y. Yang, Appl. Surf. Sci. 254 (2008) 4508.

[28] W. Q. Hong, J. Phys. D: Appl. Phys. 22 (1989) 1384.

[29] J. Tauc, F. Abelesn (ed.), Optical Properties of Solids. North Holland,1969.

[30] J. I. Pankove, Optical Processes in Semiconductors, P.36, Dover, NY, 1975. Published in aweb site: http://books.google.com/

[31] E. Burstein, Phys. Rev. 93 (1954) 632.

[32] A. A. Dakhel, Solid State Sciences 13 (2011) 1000.

[33] D. Hahn, O. Jaschhinski, H. –H. Wehmann, A. Schlachetzki, J. Electron. Mater. 24 (1995) 1357.

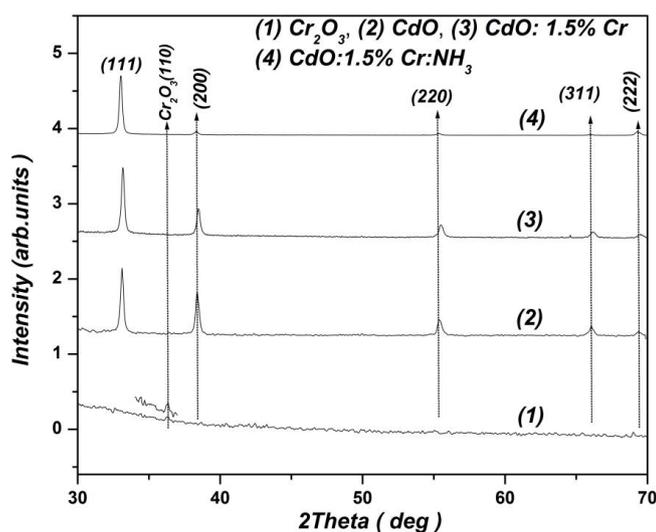[34] P. A. Wolff, Phys. Rev. 126 (1962) 405.

Fig.1 XRD patterns of 1.5% Cr-doped CdO films annealed in air and NH_3 gas with those of pure CdO and Cr_2O_3 films for comparison.
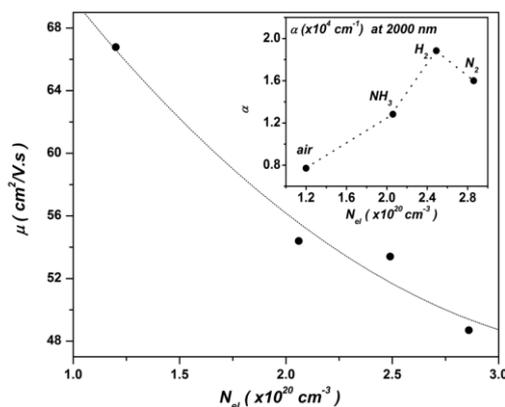

Fig.2 Dependence of carrier mobility of their concentration in 1.5% Cr-doped CdO films annealed in different gases. The inset shows the dependence of absorption coefficient α at 2000 nm on carrier concentration.
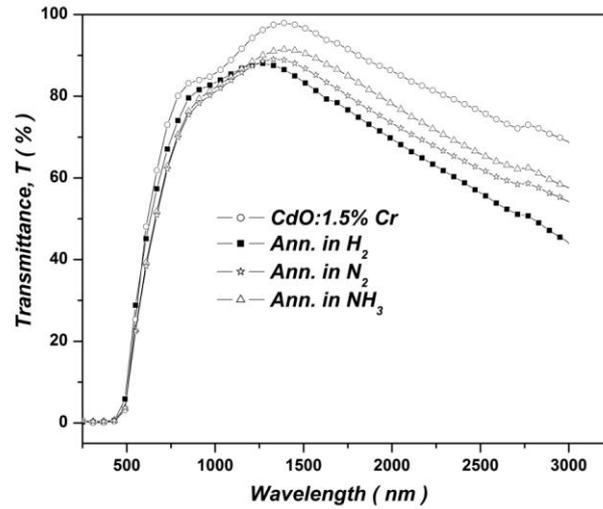
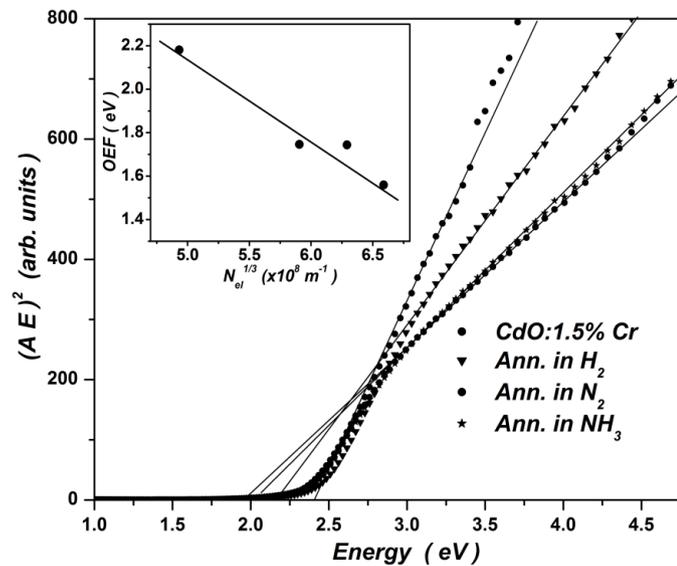**Fig.3   Spectral optical transmittance of 1.5% Cr-doped CdO films annealed in different gases.**

Fig.4   Tauc plots of 1.5% Cr-doped CdO films annealed in different gases. The asymptotic lines determine the direct bandgaps. The inset shows the $N_{el}^{1/3}$-dependence of optoelectronic function (OEF).