Structural and photoluminescence properties of CdO doped TiO$_2$
thin films prepared by pulsed laser deposition

Ghusson H. Mohammed, Ahmed M. Savory

Department of physics, Collage of science, University of Baghdad, Iraq

E-mail: ghuson.hamed@yahoo.com

Abstract

TiO$_2$ thin films have been deposited at different concentration of
CdO of (x= 0.0, 0.05, 0.1, 0.15 and 0.2) Wt. % onto glass substrates
by pulsed laser deposition technique (PLD) using Nd-YAG laser
with $\lambda$=1064nm, energy=800mJ and number of shots=500. The
thickness of the film was 200nm. The films were annealed to
different annealing (423 and 523 ) k. The effect of annealing
temperatures and concentration of CdO on the structural and
photoluminescence (PL) properties were investigated. X-ray
diffraction (XRD) results reveals that the deposited TiO$_2$(1-x)CdO$_x$
thin films were polycrystalline with tetragonal structure and many
peaks were appeared at (110), (101), (111) and (211) planes with
preferred orientation along 2$\theta$ around 27.3$^\circ$. The results of
photoluminescence (PL) emission show that there are two peaks
positioned are around 320 nm and 400 nm for predominated peak
and 620 nm and 680 nm for the small peaks.

Key words

TiO$_2$:CdO Thin Film, structural properties, photoluminescence (PL)
properties pulse laser deposition technique.

Article info.
Received: Jun. 2015
Accepted: Oct. 2015
Published: Dec. 2015

Introduction

Titanium dioxide has been one of the most extensively studied oxides
because of its remarkable optical and electronic properties [1–3]. TiO$_2$ films
have attracted attention for use in fabricating capacitors in microelectronics devices due to their
unusually high dielectric constant [4,5]. The thin films of (TiO$_2$) have
high band energy gap about (3.2 - 3.29) eV, (3.69- 3.78) eV for allowed
and forbidden direct transition respectively [6]. Crystalline TiO$_2$ film exist in three phases: rutile (tetragonal with \(a=0.4594\) nm, \(c=0.2958\) nm), anatase (tetragonal with \(a=0.3785\) nm, \(c=0.9514\) nm.), and brookite (orthorhombic with \(a=0.9184\) nm, \(b=0.5447\) nm, \(c=0.5145\) nm.), rutile being the most stable of the three, and the formation of its phase depending on the starting material, deposition method and temperature treatment. In particular, TiO$_2$ thin films can transform from amorphous phase into crystalline anatase and from anatase into rutile by changing temperature [7,8]. Rutile is usually the dominant phase in TiO$_2$ films, but in some recent work anatase-rich films have been synthesized. Many deposition methods can be used to prepare titanium oxides film: thermal [9] or anodic [10] oxidation of titanium, electron beam evaporation [11], chemical vapor deposition [12], plasma-enhanced chemical vapor deposition [13], sol–gel method [14, 15] and reactive sputtering methods [16–19]. Recently there are many applications of laser one of these applications in a thin film preparation field that called pulsed Laser deposition (PLD). The powder of precursor was mixed together using agate mortar, the mixture was then pressed into pellets (1.5 cm) in diameter and (0.2 cm) thick, using hydraulic type (SPECAC), under pressure of 5 tons. The pellets were sintered in air at temperature (773 K) for 3 h.

2. Thin films preparation of TiO$_{2(1-x)}$CdO$_x$ by PLD

TiO$_{2(1-x)}$CdO$_x$ films were deposited on glass slides substrates of (10×10 mm) at room temperature and different concentration of CdO. The glass substrate was cleaned with dilated water using ultrasonic process for 15 minute to deposit the films at room temperature then annealing treatment at (423 and 523) K by furan (Precision Model 19 Vacuum Oven made in west Germany) under vacuum (8*10$^{-2}$ mbar). Finally, deposited thin films from TiO$_2$:CdO by PLD technique using Nd:YAG with (\(\lambda=1064\) nm) SHG Q-switching laser beam at 800 mJ, repetition frequency (6Hz) for 500 laser pulse is incident on the target surface making an angle of 45° with it as shown in Fig. 1.
The distance between the target and the laser was set to (10 cm), and between the target and the substrate was (1.5 cm), under vacuum of ($10^{-3}$ mbar). The thickness of TiO$_{2(1-x)}$CdO$_x$ thin film was measured using an optical interferometer method employing He-Ne laser 0.632 µm with incident angle 45°. This method depends on the interference of the laser beam reflected from thin film surface and then substrate, the films thickness $t$ was determined using the following formula [25]:

$$ t = \frac{\lambda}{2} \cdot \frac{\Delta x}{x} $$(1)

where $x$ is fringe width, $\Delta x$ is the distance between two fringes and $\lambda$ is wavelength of laser He – Ne (632.8nm).

3. Characterization

XRD analysis using SHIMADZU 6000 X-ray diffractometer system was employed in order to obtained the crystal quality and phase structure of the films. The optical properties of TiO$_{2(1-x)}$CdO$_x$ thin films were investigated by PL spectroscopy using UV light excitation SL-174 (ELICO) Spectro Fluorometer, 150 watt Xenon Arc lamp, (EX and Em) from (200-900) nm, at photo excitation 350nm.

Results and discussion

1. Structural properties

The crystalline structure for TiO$_{2(1-x)}$CdO$_x$ recognized by study the phase of XRD for that material. Figs. (1-a, b, c) show the XRD patterns obtained for TiO$_{2(1-x)}$CdO$_x$ thin films deposited on glass substrate with thickness of 200 nm by pulse laser deposition method at different concentration of CdO $x$= (0.0, 0.05, 0.1, 0.15, 0.2) Wt. % prepare at RT and annealed to different annealing temperatures (423 and 523) K, respectively. According to American Standard for Testing Materials (ASTM) cards, the structure of thin films showed a polycrystalline tetragonal structure for TiO$_2$ of Phase classification Rutile. From Fig. 2 it can be observed that the preferred orientation was along (110) direction for Rutile. In the x-ray patterns, it is cleared that the peaks intensities increase with increasing of the doping ratio from 5 to 20%. Also, it was noticed that the all film quality improves with the increasing of annealing temperature, and appear a new peak at concentration (0.15 and 0.2) Wt. % which recognized to CdO structure that corresponding to the reflection plane of (111).
Fig. 2: The X-Ray diffraction for TiO$_2$: CdO thin films: a) at RT, b) at annealing 423K, c) at annealing 523K.

Table (1-a, b, c) gives the interplaner distance $d$, FWHM (Deg.), and grain size for the prepared samples in comparison with the standard value as in ASTM card. The structure of the TiO$_2$: CdO film has been investigated by using XRD to ensure the stoichiometry of our material. We can observe that the values of $d$ and $2\theta$ are nearly similar to that in the ASTM cards as listed in Table 1. The mean grain size of thin film calculated using the Scherer's equation [26]:

$$G = \frac{0.94 \lambda}{\beta \cos \theta}$$

where $G$ is the average crystalline grain size, $\lambda$ is the wavelength, $\beta$ represents the full-width at half maximum (FWHM) in radian and $\theta$ is the Bragg diffraction angle in degree. The grain sizes have been calculated by using Eqs. (1) and tabulated in Table 1. It is cleared from the table that $d_{hk\ell}$ and grain size increases with increasing of concentration of $x$. This implies that Cd partially substituted for Ti in TiO$_2$ structure.
Table 1: The peaks and its Bragg's angle, interplanar distance, and full width half at maximum for TiO$_2$: CdO thin films at different annealing temperatures and different concentration of CdO.

| Ts (K) | Content | $\theta$ (Deg.) | FWHM (Deg.) | Int (Arb. Unit) | $d_{\text{G.S}}$ (Å) | $d_{\text{Std.}}$ (Å) | G.S (nm) | $d_{\text{hal}}$ Exp.(Å) | $d_{\text{hal}}$ Std.(Å) | hkl |
|--------|---------|-----------------|-------------|-----------------|----------------------|---------------------|----------|--------------------------|---------------------|-----|
|        | pure    | 27.3            | 0.4542      | 25.50           | 3.2641               | 18                  | 3.2548   | (110)                    |                     |     |
|        |         | 36              | 0.5412      | 21.02           | 2.4927               | 15                  | 2.4932   | (101)                    |                     |     |
|        | 0.05    | 27.4            | 0.4578      | 24.66           | 3.2524               | 18                  | 3.2548   | (110)                    |                     |     |
|        |         | 36              | 0.6704      | 18.22           | 2.4927               | 12                  | 2.4932   | (101)                    |                     |     |
|        |         | 54              | 0.45421     | 9.25            | 1.6967               | 20                  | 1.6911   | (211)                    |                     |     |
|        | 0.1     | 27.5            | 0.43202     | 32.23           | 3.2408               | 19                  | 3.2548   | (110)                    |                     |     |
|        |         | 36              | 0.6402      | 22.70           | 2.4927               | 13                  | 2.4932   | (101)                    |                     |     |
|        |         | 54.1            | 0.6598      | 13.17           | 1.6938               | 14                  | 1.6911   | (211)                    |                     |     |
|        | 0.15    | 27.4            | 0.4255      | 25.50           | 3.2524               | 19                  | 3.2548   | (110)                    |                     |     |
|        |         | 36              | 0.4503      | 21.86           | 2.4927               | 19                  | 2.4932   | (101)                    |                     |     |
|        |         | 54.2            | 0.4023      | 17.10           | 1.6909               | 22                  | 1.6911   | (211)                    |                     |     |
|        | 0.2     | 27.35           | 0.4139      | 26.63           | 3.2582               | 20                  | 3.2548   | (110)                    |                     |     |
|        |         | 33.05           | 0.3402      | 27.75           | 2.7081               | 24                  | 2.7108   | (111)                    |                     |     |
|        |         | 36              | 0.4442      | 10.37           | 2.4927               | 19                  | 2.4932   | (101)                    |                     |     |
|        |         | 54.2            | 0.4503      | 17.66           | 1.6909               | 20                  | 1.6911   | (211)                    |                     |     |
|        | 0.2     | 27.15           | 0.3554      | 28.01           | 3.2818               | 23                  | 3.2548   | (110)                    |                     |     |
|        |         | 36.05           | 0.3791      | 24.26           | 2.4894               | 22                  | 2.4932   | (101)                    |                     |     |
|        |         | 55.2            | 0.4212      | 11.47           | 1.6627               | 21                  | 1.6911   | (211)                    |                     |     |
|        | 0.15    | 27.1            | 0.3389      | 31.09           | 3.2878               | 24                  | 3.2548   | (110)                    |                     |     |
|        |         | 33.05           | 0.2994      | 16.32           | 2.7082               | 28                  | 2.7108   | (111)                    |                     |     |
|        |         | 36.05           | 0.2949      | 18.74           | 2.4894               | 28                  | 2.4932   | (101)                    |                     |     |
|        |         | 55.6            | 0.4476      | 14.55           | 1.6516               | 20                  | 1.6911   | (211)                    |                     |     |
|        | 0.2     | 27.5            | 0.3654      | 27.73           | 3.2408               | 22                  | 3.2548   | (110)                    |                     |     |
|        |         | 36.5            | 0.4310      | 18.37           | 2.4597               | 19                  | 2.4932   | (101)                    |                     |     |
|        |         | 55.25           | 0.4867      | 13.50           | 1.6613               | 18                  | 1.6911   | (211)                    |                     |     |
|        | 0.05    | 27.5            | 0.3547      | 28.81           | 3.2408               | 23                  | 3.2548   | (110)                    |                     |     |
|        |         | 36              | 0.3097      | 24.67           | 2.4927               | 27                  | 2.4932   | (101)                    |                     |     |
|        |         | 55.25           | 0.3540      | 11.70           | 1.6613               | 25                  | 1.6911   | (211)                    |                     |     |
|        | 0.1     | 26.75           | 0.3441      | 30.79           | 3.3300               | 24                  | 3.2548   | (110)                    |                     |     |
|        |         | 35.9            | 0.2655      | 21.61           | 2.4995               | 31                  | 2.4932   | (101)                    |                     |     |
|        |         | 54.65           | 0.3655      | 15.48           | 1.6781               | 24                  | 1.6911   | (211)                    |                     |     |
|        | 0.15    | 27.65           | 0.3115      | 30.97           | 3.2235               | 26                  | 3.2548   | (110)                    |                     |     |
|        |         | 33              | 0.2867      | 12.60           | 2.7121               | 29                  | 2.7108   | (111)                    |                     |     |
|        |         | 35.85           | 0.2982      | 19.63           | 2.5028               | 28                  | 2.4932   | (101)                    |                     |     |
|        |         | 54.3            | 0.4248      | 14.40           | 1.6880               | 21                  | 1.6911   | (211)                    |                     |     |
|        | 0.2     | 27.65           | 0.2954      | 33.31           | 3.2235               | 28                  | 3.2548   | (110)                    |                     |     |
|        |         | 33.1            | 0.2212      | 17.47           | 2.7042               | 37                  | 2.7108   | (111)                    |                     |     |
|        |         | 35.25           | 0.2097      | 26.11           | 2.5440               | 40                  | 2.4932   | (101)                    |                     |     |
|        |         | 54.25           | 0.4425      | 14.04           | 1.6892               | 20                  | 1.6911   | (211)                    |                     |     |
2. Photoluminescence (PL)

Photoluminescence (PL) of the deposited TiO$_2$$_{(1-x)}$CdO$_x$ films on glass substrate at Room temperature and treated at different annealing temperatures ($T = 423$ and 523) K for one hour under vacuum with pressure ($10^{-3}$ mbr) and different concentration of CdO at $x = (0.0, 0.05, 0.1, 0.15, 0.2)$ wt.% were measured. Fig. (3-a, b, c) shows the PL spectrum of the TiO$_2$$_{(1-x)}$CdO$_x$ films at room temperature and annealed to different annealing temperatures and different concentration of CdO. Typical luminescence behavior with two emission peaks, UV PL characteristics of TiO$_2$$_{(1-x)}$CdO$_x$ films showed strong relation to the temperature. The first peak in PL spectra between (320-400) nm corresponds to the direct recombination between electrons in the conduction band and holes in the valence band [27]. In all the samples (pure and dopant) a broad peak was also observed at a lower energy or visible region (second peak). The intensity of the two peaks increases markedly with the increase of concentration, due to the large exciton bending energy of TiO$_2$$_{(1-x)}$CdO$_x$. Higher energy (shorter wavelength) excitation photons cause more phonons to be emitted before luminescence occurs. If the excitation energy is less than the energy difference between the ground state and the first excited state, then no optical absorption will occur, resulting in no PL. The PL emission might have close relation with the luminescence of the recombination of photo induced electrons and holes, the free and self- trapped electron-hole pair or excitons, which possibly resulted from the nointegrality of nano-sized TiO$_2$ crystallite such as the lattice distortion and surface oxygen deficiencies. However, in thin films, the broad band visible emission at (620-680) (nm) this luminescence could be due to the self-trapped excitons of the charge transfer process. The Table 2 shows the peak values and the energy of the luminescence spectrum of all samples. It is observed from this table The value of the optical energy gap increases with increasing of Ta for all samples, this is due to the growth of grain size and the decrease in defect states near the bands and these in turn increase the value of $E_g$. The optical energy gap decreases with increasing concentration this is due to the increase of the density of localized states in the $E_g$ which cause a shift to lower values.

Conclusion

Pure TiO$_2$ and TiO$_2$$_{(1-x)}$CdO$_x$ thin films were deposited by PLD technique on glass substrates with different concentration of CdO at RT and annealed to different annealing temperatures (423 and 523) K. The resulting of TiO$_2$$_{(1-x)}$CdO$_x$ films were characterized by XRD measurement and PL properties. X-ray diffraction (XRD) results reveals that the deposited TiO$_2$$_{(1-x)}$CdO$_x$ thin films were polycrystalline with tetragonal structure of Phase classification Rutile. Annealing the films in vacuum for one hour increases the grain size and noticed that the all film quality was improved and appear a new peak at content of (0.15 and 0.2) Wt. % which recognized to CdO structure. From PL analysis it is observed two emission peaks, UV PL characteristics of for pure TiO$_2$ and doped TiO$_2$ with CdO and the intensity gradually increases by increasing the doping.
Fig. 3: Photoluminescence spectra for TiO$_2$: CdO thin films: a) at RT, b) at annealing 423K, c) at annealing 523K.
Table 2: The peak values and the energy of the luminescence spectrum of all samples.

| Ts (K) | content x | wavelength (nm) | \( E_g \) (eV) | wavelength (nm) | \( E_g \) (eV) |
|--------|------------|----------------|--------------|----------------|--------------|
|        |            | first peak     |              | second peak    |              |
| RT     | 0          | 350            | 3.543        | 627            | 1.978        |
|        | 0.05       | 355            | 3.493        | 630            | 1.968        |
|        | 0.1        | 360            | 3.444        | 634            | 1.956        |
|        | 0.15       | 365            | 3.397        | 636            | 1.950        |
|        | 0.2        | 370            | 3.351        | 639            | 1.941        |
|        | 0          | 332            | 3.735        | 624            | 1.987        |
|        | 0.05       | 340            | 3.647        | 626            | 1.981        |
|        | 0.1        | 346            | 3.584        | 628            | 1.975        |
|        | 0.15       | 353            | 3.513        | 630            | 1.968        |
|        | 0.2        | 361            | 3.435        | 633            | 1.959        |
| 423    | 0          | 330            | 3.758        | 620            | 2.000        |
|        | 0.05       | 334            | 3.713        | 622            | 1.994        |
|        | 0.1        | 340            | 3.647        | 624            | 1.987        |
|        | 0.15       | 344            | 3.605        | 627            | 1.978        |
|        | 0.2        | 352            | 3.523        | 629            | 1.971        |

References

[1] N.S.P. Bhutanese, J. Gopalakrishnan, J. Mater. Chem. 7, (1997) 2297.
[2] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735.
[3] G.S. Oehrlein, J. Appl. Phys. 59 (1986) 1587.
[4] C.N. Wilmsen, Physics and Chemistry of Compound III–V Semiconductor Interfaces, Plenum Press, New York, (1985).
[5] L. Messick, J. Appl. Phys. 47 (1976) 4949.
[6] R. Mechikh, R. Bensaha, M. J. Condensed Mater, 7 (2006) 54.
[7] Y. Leprince-Wang and K. Yu-Zhang, Surf. Coat. Technol. 140 (2001) 155–160.
[8] Altin Gjevori, "Phase Formation of Photoactive TiO_2 Thin Films by Metal Plasma Immersion Ion Implantation and Deposition", M.Sc. Thesis, University of Tirana, Faculty of Natural Sciences, (2010).
[9] B. Morris Henry, US Patent 4, 200 474 (1978).
[10] M.R. Kozlowski, P.S. Tyler, W.H. Smyrl, R.T. Atanasoki, J. Electrochem. Soc. 136 (1989) 442.
[11] M. Lottiaux, C. Boulesteix, G. Nihoul, F. Varnier, F. Flory, R. Galindo and Pelletier., Thin Solid Films 170 (1989) 107.
[12] K.S. Yeung, Y.W. Lam, Thin Solid Films 109 (1983) 405.
[13] L.M. Williams, D.W. Hess, J. Vac. Sci. Technol. A 1 (1983) 1810.
[14] K.A. Vorotilov, E.V. Orlova, V.I. Petrovsky, Thin Solid Films, 207 (1992) 180.
[15] M. Gartner, C. Parlog, P. Osiceanu, Thin Solid Films, 234 (1993) 561.
[16] M.H. Suhail, G. Mohan Rao, S. Mohan, J. Appl. Phys. 71 (1992) 1421.
[17] L. J. Meng, M. Andritschky, M.P. dos Santos, Thin Solid Films, 223 (1993) 242.
[18] G. Lazar, I. Vascan, Rom. J. Phys., 43 (1998) 571.
[19] H. Tang, K. Prasad, R. Sanjines, P.E. Schmid, F. Levy, J. Appl. Phys. 75, 4 (1994) 2042.
[20] H. M. Smith, A. F. Turner, Appl. Opt. 4, (1965) 147.
[21] Dijkkamp, T. venkatesan, X. D. Wu, S.A. shareen, N. Jisnari, Y. (1987).
[22] R. Ferro and J. A. Rodriguez, Sol. Energy Mater. Sol. Cells 64, (2000) 363.
[23] T. K. Subramanyam, S. Uthanna, B. Srinivasulu Naidu, Mater. Lett. 35 (1998) 214.
[24] P. R. Patil, P. S. Patil, C. D. Lokhande, Ind. J. Phys. 266 (1995) 14.
[25] Y. M, L. Qi, J. M, H. Cheng, Adv. Mater., 16, 1023, (2004).
[26] A.L. Patterson, A. L. Phys. Rev, 56 (1939) 978.
[27] J. Liqiang, S. Xiaojun, X. Baifu, W. Baiqi, C. Weimin, F. Honggang, Journal of Solid State Chemistry, 177 (2004) 3375.