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Effect of Thermal Annealing on Photoluminescence Characteristics of Titanium Dioxide Thin Films Doped with Copper Oxide by Pulsed-Laser Deposition

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In this work, titanium dioxide thin films were deposited on glass substrates and doped with copper oxide at different concentrations (0.0, 0.05, 0.1, 0.15 and 0.2 wt.%) by pulsed-laser deposition technique followed by thermal annealing at different temperatures (423 and 523 K) to study the effects of annealing temperature on their photoluminescence characteristics. The results of photoluminescence emission showed that there are two peaks positioned at 320 and 400 nm for predominated peak and at 620 and 680 nm for the small peaks. It was found that the energy band gap of the prepared samples was decreasing with increasing the content of copper oxide dopants in titanium dioxide thin films regardless the value of annealing temperature.

Keywords: Titanium dioxide; Copper oxide; Photoluminescence; Thermal annealing

1. Introduction

In the processes of heterogeneous catalysis, surface area plays the main role. In the processes of photocatalysis, the redox potential of charge carriers and the selectivity of the catalyst surface are important [1,2]. Recently, nanostructured materials have been considered for these purposes. The most popular of these is titanium dioxide [3]. TiO_2 is a semiconductor whose photocatalytic properties deteriorate under visible light due to its wide band gap [4]. It is known that doping increases the photocatalytic activity of TiO_2 upon irradiation with visible light. The nature of the dopant ion also affects this activity since the dopants can be interstitial, substitutional, or both in the case of incorporation [5]. Different locations have a different effect on the properties of titanium dioxide [6]. A comparison of the effectiveness of photocatalytic decomposition or synthesis of organic compounds is difficult since doping is carried out using different methods (sol–gel, solid reaction/mechanical activation, chemical vapor deposition, *etc.*), in which various precursors of metal ions are used [6-8]. This can also affect the photocatalytic activity of the resulting samples.

Titanium dioxide has been one of the most extensively studied oxides because of its remarkable optical and electronic properties [9-11]. Titanium dioxide films have attracted attention for use in fabricating capacitors in microelectronics devices due to their unusually high dielectric constant [12]. Titanium dioxide thin films have high band energy gap of 3.2-3.29 eV and 3.69-3.78 eV for allowed and forbidden direct transition, respectively [13]. Crystalline titanium dioxide film exists 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). Amongst the three phases, the rutile is the most stable and its formation depends on the starting material, deposition method and treatment temperature. In particular, titanium dioxide thin films can transform from amorphous phase into crystalline anatase and from anatase into rutile by changing temperature [14,15]. Rutile is usually the dominant phase in titanium dioxide films, but in some recent work, anatase-rich films have been synthesized. Many deposition methods can be used to prepare titanium oxides film: thermal [16] or anodic [17] oxidation of titanium, electron beam evaporation [18], chemical vapor deposition (CVD) [19], plasma-enhanced chemical vapor deposition PE-CVD [20], plasma-induced bonding (PIB) [21], sol-gel method [22,23], reactive sputtering methods [24-27] and pulsed-laser deposition (PLD) technique [28,29], which was first used by smith and Turner in 1965 to prepare semiconductor and dielectric thin films and was established due to the work of Dijkkamp and coworkers [30] on high-temperature superconductors in 1987.

Copper oxide (CuO) is p-type semiconductor with indirect energy band gap of 1.4-1.8 eV. It is efficiently used for water splitting due to the photocatalytic activity as its conduction and valence bands narrowly straddle the water redox potentials. However, it shows relatively lower efficiency to

convert sunlight into hydrogen [31-33]. It may be expected that CuO is an ideal material as a solar cell due to its energy band gap (1.4-1.8eV), which includes the ideal value of solar radiation conversion (1.5eV). However, due to the ohmic losses and overpotentials in photoelectrical and photoelectrochemical systems, this material does not keep this position [34,35].

2. Experimental Part

Titanium dioxide from NanoShell Company with purity of 99.99% and cadmium oxide with purity of 99.99% were mixed at different concentrations of cadmium oxide (0.0, 0.05, 0.1, 0.15 and 0.2 wt.%). The powder of precursor was mixed together using agate mortar and the mixture was then pressed into pellets of 1.5 cm in diameter and 0.2 cm in thickness, using SPECAC hydraulic press under pressure of 5 tons. The pellets were sintered in air at temperature of 773 K for 3 hours.

The $TiO_{2(1-x)}CuO_x$ films were deposited on 10×10 mm glass substrates at room temperature and different concentrations of CuO. The glass substrates were cleaned with diluted water using ultrasonic process for 15 minutes to deposit the films at room temperature then anneal them at 423 and 523 K by a furnace under vacuum ($8x10^{-2}$ mbar). Finally, thin films of TiO_2:CuO were deposited by PLD technique using a 1064nm Q-switched Nd:YAG laser with pulse energy of 800 mJ, repetition frequency of 6 Hz for 500 laser pulses incident on the target surface making an angle of 45°, as shown in Fig. (1).

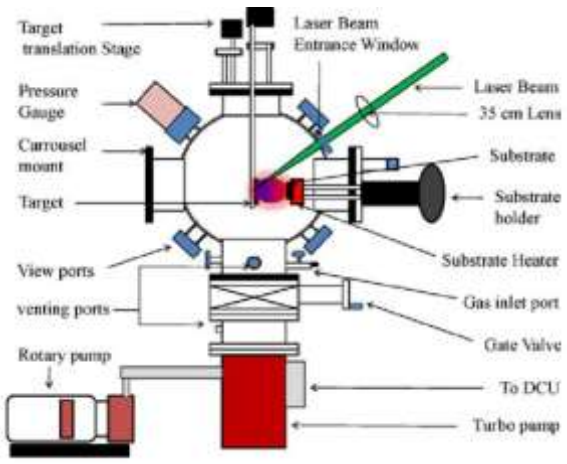


Fig. (1) Experimental setup of PLD system used in this work

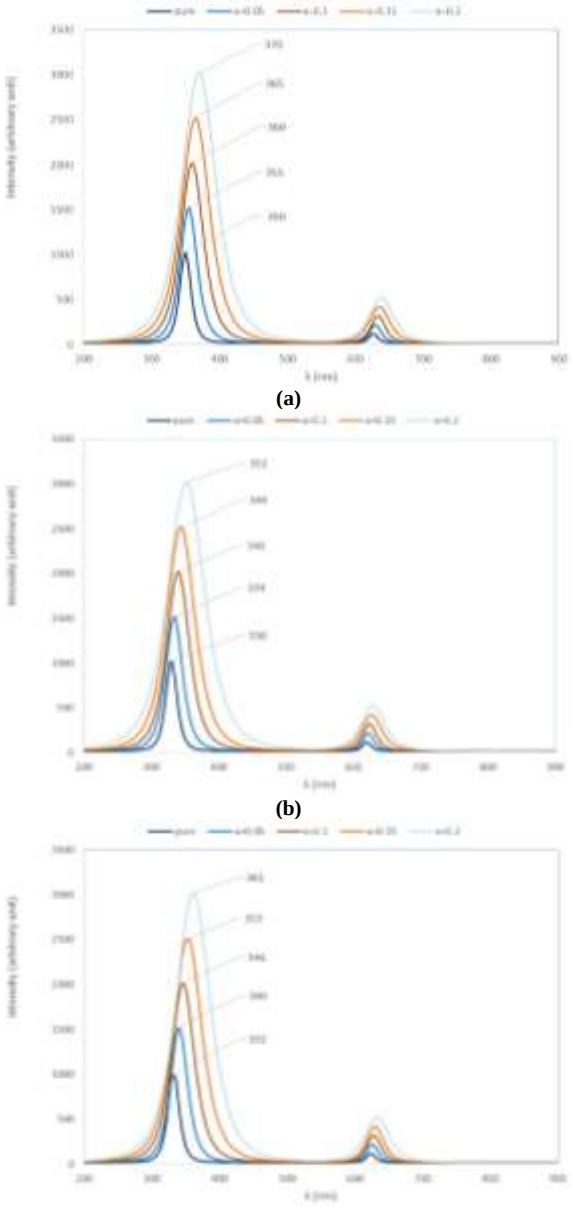
The distance between the target and laser was set to 10 cm, and between the target and substrate was 1.5 cm, under vacuum of 8×10^{-2} mbar. The thickness of $TiO_{2(1-x)}CuO_x$ thin films was measured using an optical interferometer method employing 632.8nm He-Ne laser with incident angle of 45°. This method depends on the interference of laser beam reflected from thin film surface and then substrate.

The photoluminescence spectra were recorded using Edinburgh Instrument model FLS920 in the spectral tange of 200-1000nm.

3. Results and Discussion

The photoluminescence (PL) of the 200nm-thick $TiO_{2(1-x)}CuO_x$ films deposited at room temperature and different concentrations of CuO (x=0.0, 0.05, 0.1, 0.15, 0.2 wt.%), and annealed at different temperatures (423 and 523 K) for one hour under vacuum pressure of $8x10^{-2}$ mbr were measured using 150 W xenon arc lamp, in the range of 200-1000 nm at photo-excitation wavelength of 350 nm.

Figure (2) shows the photoluminescence spectra of the $TiO_{2(1-x)}CuO_x$ films prepared at room temperature and different concentrations, and annealed at different temperatures.



(a)

(b)

(c)

Fig. (2) Photoluminescence spectra for CuO-doped TiO_2 thin films (a) at room temperature, (b) at annealing temperature of 423K, and (c) at annealing temperature of 523K

Typical luminescence behavior with two emission peaks was observed and the UV photoluminescence characteristics of $TiO_{2(1-x)}CuO_x$ films showed strong relation with the temperature. The first peak in photoluminescence spectra between 320-400 nm corresponds to the direct recombination between electrons in the conduction band and holes in the valence band.

In all samples (undoped and doped), a broad peak was also observed at a lower energy or visible region (the second peak). The intensity of the two peaks apparently increases with the increase of concentration due to the large exciton bending energy of $TiO_{2(1-x)}CuO_x$ compound. Higher energy (shorter wavelength) excitation photons cause more phonons to emit before the occurrence of luminescence. If the excitation energy is lower than the energy difference between the ground and first excited states, then no optical absorption will occur, and hence no photoluminescence will result.

Table (1) Peak wavelengths of photoluminescence spectra and energy band gap of the prepared samples

T_s (K)	Content (x)	Wavelength (nm)	E_g (eV)
		First peak	
R.T.	0	350	3.543
	0.05	355	3.493
	0.1	360	3.444
	0.15	365	3.397
	0.2	370	3.351
423	0	332	3.735
	0.05	340	3.647
	0.1	346	3.584
	0.15	353	3.513
	0.2	361	3.435
523	0	330	3.758
	0.05	334	3.713
	0.1	340	3.647
	0.15	344	3.605
	0.2	352	3.523

T_s (K)	Content (x)	Wavelength (nm)	E_g (eV)
		Second peak	
R.T.	0	627	1.978
	0.05	630	1.968
	0.1	634	1.956
	0.15	636	1.950
	0.2	639	1.941
423	0	624	1.987
	0.05	626	1.981
	0.1	628	1.975
	0.15	630	1.968
	0.2	633	1.959
523	0	620	2.000
	0.05	622	1.994
	0.1	624	1.987
	0.15	627	1.978
	0.2	629	1.971

The photoluminescence emission may have close relation with the luminescence of the recombination of photo-induced electrons and holes. The free and self-trapped electron-hole pairs or excitons are possibly resulted from the non-integrality of nano-sized TiO_2 crystallites such as the lattice distortion and surface oxygen deficiencies. However, in thin films, the broad visible emission band at 620-680 nm could be attributed to the self-trapped excitons of the charge transfer process. Table (1) shows the peak wavelengths of photoluminescence spectra and energy and gaps of all samples prepared in this work.

4. Conclusion

In concluding remarks, $TiO_{2(1-x)}CuO_x$ thin films were deposited by PLD technique on glass substrates at different concentrations of CuO at room temperature and then annealed at different temperatures (423 and 523K). Annealing of these films in vacuum for one hour improves the film quality as the doping level is increased. Two emission peaks were observed from photoluminescence analysis, UV photoluminescence characteristics of for undoped and CuO-doped TiO_2 and the intensity gradually increases by increasing the doping level.

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