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International Journal of Nano Studies & Technology (IJNST)
ISSN:2167-8685

Photoelectric Characteristics of Nano TiO_2 Film Prepared By Spraying Pyrolysis Method

Review Article

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Abstract

The nanocrystalline TiO_2 (nc TiO_2) film was prepared by spraying pyrolysis method. Starting material for the synthesis was $TiCl_4$. Phase compositions and crystalline sizes were examined by pattern of XRD, and surface morphology of the thin film was analyzed by SEM and AFM. Optical characteristics were examined by UV – Vis and luminescent spectra (PL). Electric characteristics were examined by measuring resistance changing of films versus temperature. The experimental data showed that the forming films had nanostructure and typical photoelectric characteristics of nano TiO_2 material which is similar to the ones prepared by other preparing methods. IF compared to others, this preparing method has such as simple equipments, inexpensive and available materials; so it is suitable for mass production.

Keywords: Nano TiO_2 film; Spraying Pyrolysis Method.

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Received: April 07, 2015
Accepted: May 06, 2015
Published: May 08, 2015

Citation: Cuong Tran Kim (2015) Photoelectric Characteristics of Nano TiO_2 Film Prepared by Spraying Pyrolysis Method. *Int J Nano Stud Technol.* 4(1), 78-83. **doi: http://dx.doi.org/10.19070/2167-8685-1500015**

Introduction

Nano titanium oxide has a lot of applications in real life. It is used to make dye in industry to produce paint, plastic, paper and food products. TiO_2 has been even covered on interior furniture to create reflected light effects which increase their beauty, etc. Together with development of nano material technology, at present, there are important applications of nano (nc) TiO_2 including photocatalysis, solar cells, photon and photoelectron devices, etc. With oxidation potential is 3.2 eV, under effect of ultraviolet light (UV), nc TiO_2 can decompose very strong toxic wastes in environment.

TiO_2 was used as an insulating gate on the field effect transistor (FET) [15], to make detectors for measuring nuclear radiations [2], and to make luminescence devices [4]. When doping more appropriate impurities, it will create energy levels of Ea located in the bandgap. If electrons simultaneously jump from excited levels to elementary energy levels, the material shall generate desired radiations. The change of color windows act based on this principle. The impurities energy levels can be controlled by electric field; therefore, we have color changing instantaneously depending on the control of the electric field [10, 20]. TiO_2 was also used to make anti reflexing layers help enhancement of efficiency of photosemiconductor amplifiers (laser) GaInAs/AlGaInAs [12]. Because TiO_2 has very large refractive index, fiber optic cables or optic windows covered this material, which acts based on continuous reflection principle, will produce total reflect, which will minimize the loss of light (sign).

There have been different methods used to prepare nano materials and nano films from relatively simple to rather complex including physics methods (Physical vapor deposition – PVD), chemical methods (Chemical vapor deposition – CVD) and many others such as physics and chemical combined method or combined different methods.

Spraying pyrolysis method (SP) is one of the most simple and economic methods to prepare oxide metals. Using nano TiO_2 films prepared by SP method and using inexpensive materials can enhance applied ability of this material [1]. Besides the simplicity of the method, low cost with a minimum amount of waste, SP process even permits to prepare cover layers with large areas and easily apply for industrial manufacture [8]. This is remarkable advantage of SP method compared to other methods.

SP method has been used by many authors to prepare nano TiO_2 films including single atom films and polyatomic films from different starting salts. Actually, the authors [18] sprayed pyrolysis liquid mixture of titanium and niobium peroxo-hydroxo on quartz substrate to prepare oxygen sensitive sensor. Another authors [5] prepared TiO_2 films and carbon doped TiO_2 powder using starting material was titanium-tetraisopropoxide, the obtained films have anatase single phase structure, the average size of crystalline particles was ~ 160 nm. Additionally, the authors [1] prepared

TiO_2 films on glass substrate using titanium (IV) isobutoxide [Ti $((CH_3)_2CHCH_2O)_4$] as starting material. Also, the authors [19] prepared TiO_2 films on glass substrate using starting material of $C_{10}H_{14}O_5Ti$, the obtained films have the crystalline particle size from 30nm to 50nm. The authors [17] prepared TiO_2 films by starting materials of $TiCl_3$ solution. The authors [4] prepared TiO_2 films by using titanium diisopropoxide as starting material, the average size of crystalline particles was ~ 210nm.

Experiments

Materials

$TiCl_4$ was prepared into solution with concentrations ranging from 0.025 to 0.15mol/dm^3 (M). The solution was sprayed with atmosphere-pressing pressure 1.5 at. Substrates were made by optical glass with thickness of 1.2mm. Substrate temperatures were studied ranged from 340°C to 460°C.

Apparatus

X-ray diffraction patterns (XRD) of nanocrystalline TiO_2 films were measured by a D8-AVANCE BRUKER X-ray diffractometer using Cu Kα radiation (k = 0.1542nm) with 0.02°/sec scan rate. Field effect scanning electron micrographs (FESEM) were taken with a FESEM HITACHI S4800 field effect scanning electron microscope. Atom force micrographs were taken with a Multimode-VEECO-USA atom force microscope. UV-Vis absorption spectra were measured by a Shimadzu UV-Vis 2540 absorption spectrometer. Luminesce spectra were measured by a FL 3-22 Jobin – Yvon – Spec., USA.

Apparatus for preparing nano TiO_2 by spraying pyrolysis method

This apparatus are self-prepared. Scheme of nano TiO_2 film preparing system by spraying pyrolysis deposition method was showed in Figure 1. Temperature controlling system used digital technology of OMRON company with degree of displaying accuracy of 1°C. Steam pressure was controlled by two compressed valves of UniD800 (Taiwan). Spraying frequency was controlled by electronic IC system which may control all of pulse to alter not only spraying time but also pausing time.

Results and Discussion

Structure and morphology of nano TiO_2 films

The crystalline phase of ellipsoidal TiO_2 was characterized by X-ray diffractometer. Figure 2 shows the film XRD pattern deposited from spraying pyrolysis deposition method at 380°C with solution concentrate of $TiCl_4$ = 0.03M. The XRD pattern shows that Bragg reflections were very clear at typical diffraction angles 2θ = 25.4°, 38.8°, 48.0° and 55.0° corresponding to crystalline planes: (101), (112), (200) and (211), they were the same as results of the authors [11]. All of the films had single phase anatase structure.

Figure 3 shows the XRD patterns of the films prepared at different substrate temperatures at the same experimental condition. The XRD patterns showed that at the studying temperature range of 340 – 460°C, all of the formed films had single phase anatase structure.

The surface morphologies of the film deposited at 450°C are shown in Figure. 3 and 4. From the profiles, it can be observed that the film is porous nanostructure with the average grain size of about 20nm. This relates to evaporation process of solvent and semi-finished product in the pyrolysis process from starting material. Image of Scanning electron micrograph (SEM) of the typical pattern prepared by solution concentrate 0.1 M and at temperature of 450°C is shown in Figure. 4 and its atomic force micrograph (AFM) are shown in Figure 5.

The SEM shows the particles are distributed relatively homogeneously and mesoporously. This result agrees with the SEM of nano TiO_2 film of authors prepared by different methods [6, 7].

The AFM image shows that size of crystalline particles obtained in this work relatively uniform at the range ~ 10 – 15 nm, roughness of film was about 100nm, there were a lot of holes inside

Figure 1. Scheme of nano TiO_2 film prepared system by spraying pyrolysis method.

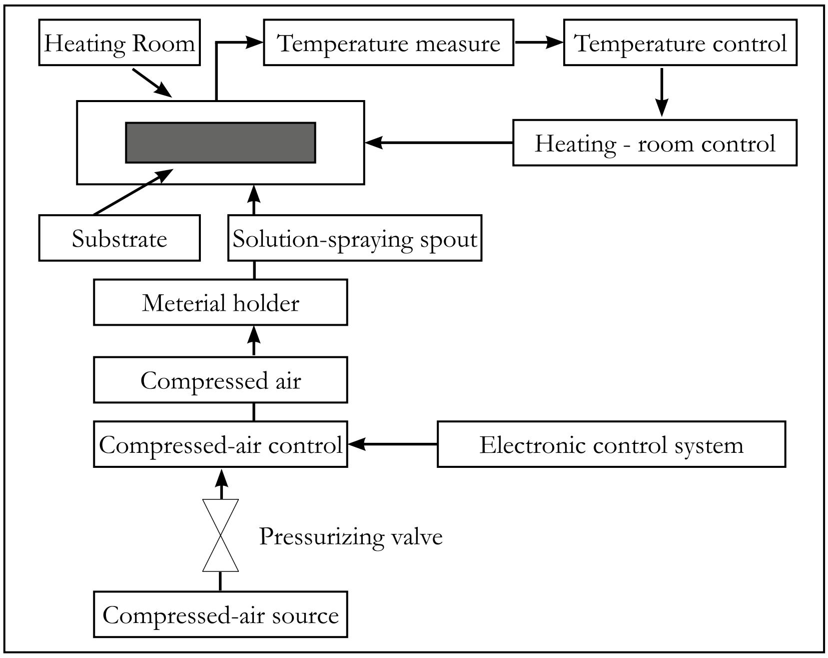


Figure 2. The XRD pattern of TiO_2 film prepared from spraying pyrolysis deposition method at 380°C.

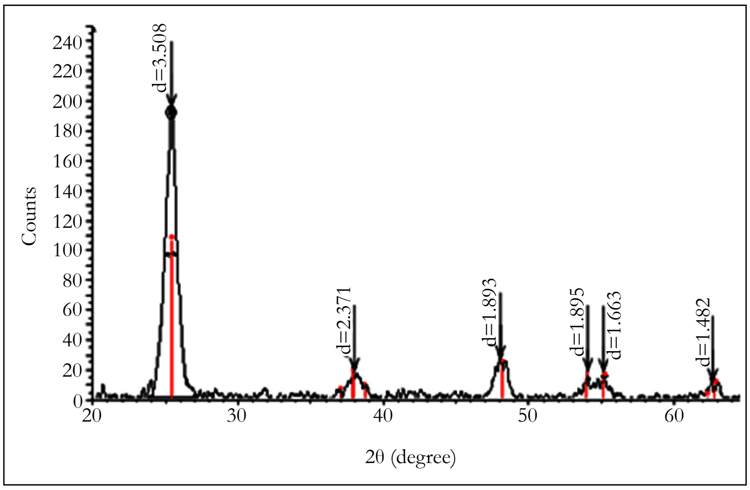


Figure 3. The XRD patterns of TiO_2 films prepared from spraying pyrolysis deposition method at different substrate temperatures

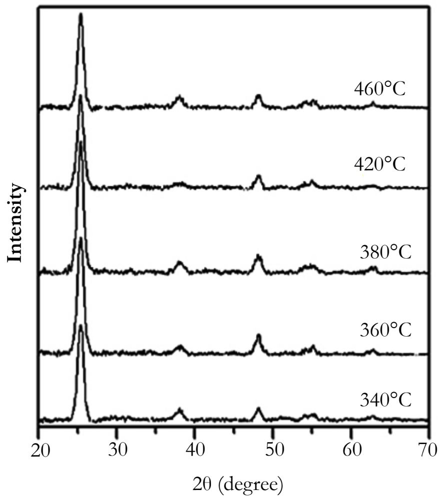


Figure 4. SEM image of nano TiO_2 film deposited from spraying pyrolysis deposition method at substrate temperature of 450°C

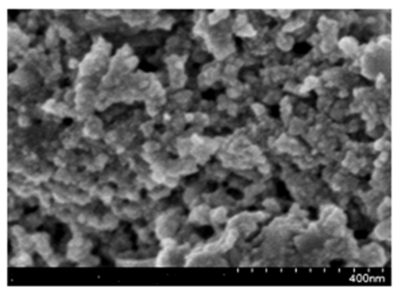
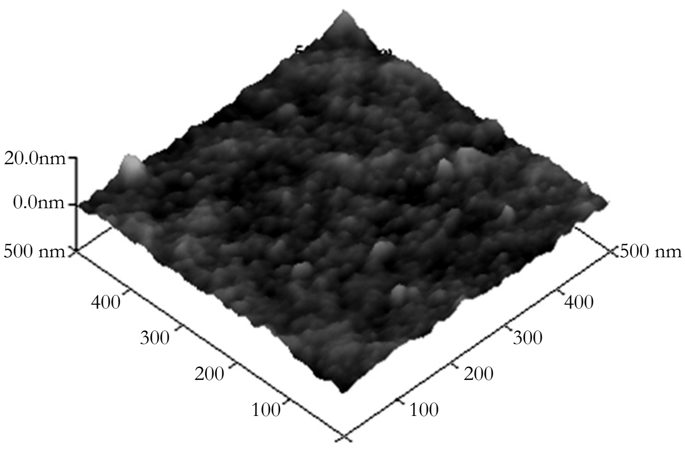


Figure 5. AFM image of nano TiO_2 film deposited from spraying pyrolysis deposition method at temperature of 450°C.



the film. Combined with SEM image, it can be seen that sizes of holes varied on a large scale – in range from ~ 20 nm to ~ 200 nm. The formed films had a very porous structure, so they may have high efficiency on applications of photocatalysis and photo-electrochemical dye sensitized solar cells.

Optical characteristics of nano TiO_2 films

Figure 6 shows the absorption spectrum of nano crystalline TiO_2 films prepared at substrate temperature of 450°C and solution concentration of 0.1M. Absorption of the films was a function of light wavelength, it slowly increased according to decreasing of wavelength in visible light range, but in ultra violet range absorption coefficient increased very fast corresponding with level transitions band – band of electrons from valence band to conduction band of nano TiO_2. The shape of absorption spectrum obtained here was the same as that of the authors prepared from $TiCl_3$ by the same SP method [17], or from $TiCl_4$ and $Ti(SO_4)_2$ by other methods [3, 23, 24], or from commercial nano TiO_2 powder by doctor blade method [22], or of nano TiO_2 particles prepared by hydrolysis method $TiCl_4$ [14].

Adsorption edge was determined by linear extrapolation of absorption coefficient α in absorption range to value 0 as well as the authors made [16]. Obtained result was adsorption edge at 370 nm, corresponding with photon energy at 3.35 eV.

From absorption spectrum, we can calculate bandgap size from expression for fundamental adsorption coefficient:

$$\alpha(h\gamma) = A[h\gamma - (Eg \pm h\gamma_f)]^2 \text{ ------ (1)}$$

Where hγ denotes energy of photon, Eg is bandgap energy of semiconductor, hγf denotes energy of phonon, A is constant.

The authors [6, 9, 17, 19. 23] calculated bandgap size for nano TiO_2 according to Tauc model in the range of high absorption coefficient [9] by expression:

$$\alpha = \frac{A(h\gamma - E_g)^{n/2}}{h\gamma} \text{ ------- (2)}$$

A is constant which is not dependent on energy of photon, but according to the authors [6] then A is absorption coefficient which is dependent on energy of photon for the case of nano TiO_2; n = 1 for allowed direct level transitions, n = 4 for allowed indirect level transitions, n = 3 for forbidden indirect optical level transitions.

Graph expresses $(\alpha h\gamma)^{1/2}$ that is calculated according to absorption spectrum of nano TiO_2 film in Figure 7 on photon energy of incident light was showed on figure 6. Bandgap size ~ 3.35 eV was obtained by extrapolating linearly at the absorption range with high photon energy to value α = 0. This result was in the value range of other authors [3, 23, 24].

Obtained E_g value was larger than that of anatase TiO_2 bulk (3.2 eV). The cause may not be by nonstoichiomatric composition of nano TiO_2 film, since the nonstoichiomatric composition leads to decrease in bandgap size. According to [21], a nonstoichiometry only leads to creating oxygen vacancies (Ti^{3+}) acting as trap levels in TiO_2 layers but does not lead to increasing in bandgap size. This occurs similarly to doped semiconductor. All of the authors reckoned that the increase of bandgap size for nano TiO_2 prepared by different methods with different starting materials was due to quantization of size [14, 16, 22, 23]. The obtained value was in the value range of other authors for nano TiO_2 films prepared by SP method from different starting materials: E_g = 3.31 – 3.36 eV from Titanyl acetylacetonate (TiAcAc) [19]. Direct bandgap size E_g = 3.1 eV from $TiCl_3$ [17]. E_g = 2.99; 3.30 và 3.32 eV from solution of ethanol titanium diisopropoxide, corresponding to substrate temperatures were 250, 400 and 500°C [3]. E_g ~ 3.8 eV from titanium (IV) isobutoxide [1]. Indirect optical bandgap size E_g = 3.39 – 3.42 eV and direct optical bandgap size E_g = 3.67 – 3.72 eV [9].

Figure 8 shows luminescent spectrum of nano TiO_2 film was excited at wavelength of 330nm. Luminescent spectrum had maximum peak at wavelength of 394.5nm.

In nano TiO_2 material system, luminescent level transitions were band–band level transitions, band–dopant and exiton recombinations. The peaks on luminescent spectrum corresponded with optical level transitions. Maximum of luminescent spectrum stretched in large range may be due to the overlapping spectrum peaks. Luminescent spectrum of anatase nano TiO_2 patterns was thought to belong to exiton traps, oxygen vacant and surface states [13].

UV-Vis adsorption and luminescent spectra of nano TiO_2 film here had the same shape as nano TiO_2 films prepared by other methods [16, 23, 24].

Electric characteristics of nano TiO_2 films

To study electric characteristics of obtained films, the change of film resistance versus temperature was measured. Studying -temperature range is from room temperature to 450°C. At room temperature, the film was almost insulated. From about 150°C, the film started electric-conducting and then its resistance gradually decreased with temperature increase. This is a typical rule of semiconductor materials. This change rule is shown in Figure 9. From the graph of ln(1/R) versus temperature inverse, here R is resistance of film, we can determine two energy levels:

– At high temperature range, conductivity of film increased due to only heat excitations to jump electrons from valence band to conduction band – this is a range relating to intrinsic conductivity of semiconductor – has value of~3.32 eV, corresponding with bandgap energy of nano TiO_2. This result was relevant to the calculated results E_g from UV–Vis absorption spectrum measurement (~ 3.35 eV).

– At low temperature range, conductivity of film was mainly because carriers were created from dopants ionized – this was a range of conductivity as dopants for extrinsic semiconductor – had value of ~ 0.69 eV, corresponding with dopant level, it may be due to unexpected dopants. This was deep level so it had large carrier catching cross-section. These deep centres relate to luminescent process of TiO_2, because deep centres usually act as recombinations or effective traps and control life-time of carriers.

Figure 6. UV-Vis absorption spectra of nano TiO_2 film prepared at 450°C.

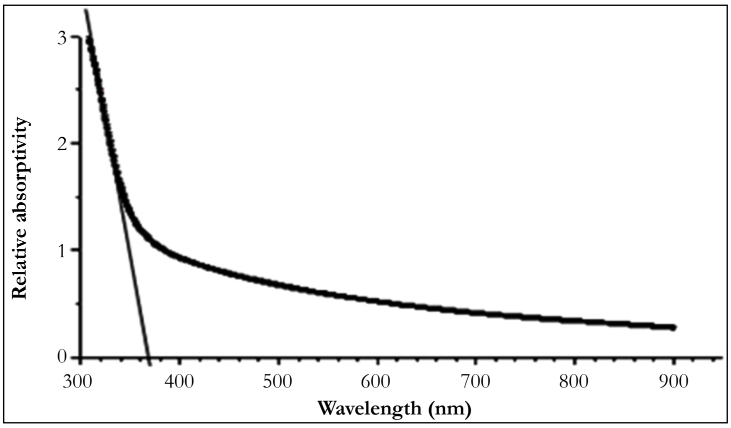


Figure 7. $(\alpha h\nu)^{1/2}$ as a function of hν for the TiO_2 film calculated according to absorption spectra of nano TiO_2 in figure 6.

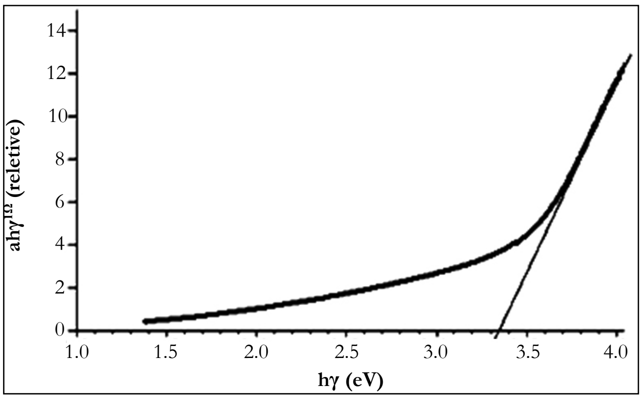


Figure 8. Luminescent spectrum of nano TiO_2 film excited at wavelength 330nm.

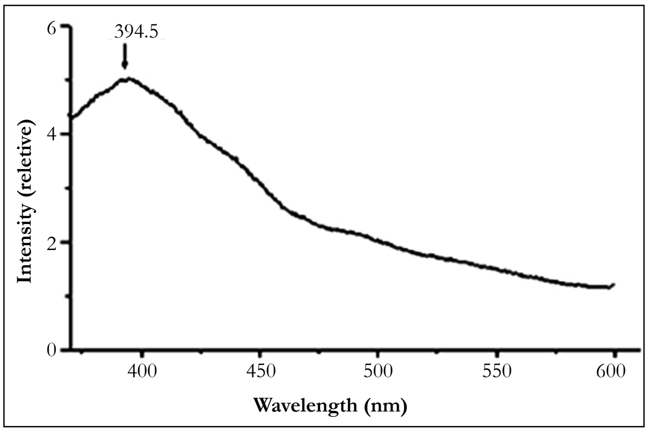
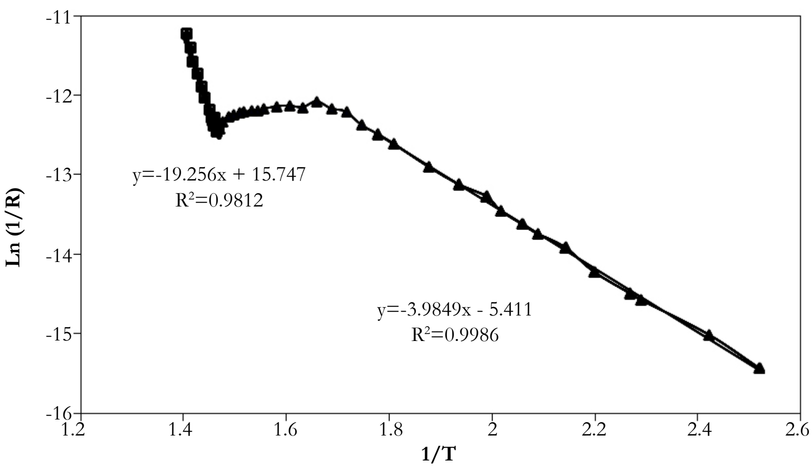


Figure 9. The dependence of resistance of nano TiO_2 film on temperature.



Conclusion

Nanocrytalline TiO_2 films were prepared by spraying pyrolysis method. Experimental results show that at substrate temperature ranging from 340°C to 460°C with solution concentration from 0.025 to 0.15M, all of them gave TiO_2 films condensed on glass substrate. These were anatase single phase, nanocrytalline TiO_2 films with high crystalline quality and cleanliness, equivalent to other expensive prepared methods include comparison with commercial products. The films had mesoporous structure with average sizes of crystalline particles were at range 7–10nm which were lightly dependent on starting-solution concentration and prepared temperature. This method gave nano TiO_2 films with small particle size and high stability in comparison with other methods.

Characteristic studying results showed that the obtained nano TiO_2 films sufficiently exposed typical photoelectric characteristics of TiO_2 semiconductor material. Characteristic parameters such as absorption spectrum, luminescent spectrum, bandgap size were suitable and equivalent to data of other authors.

Therefore spraying pyrolysis method with simple equipments, used inexpensive and available materials enables to prepare nano TiO_2 films with high quality to meet demands of fundamental and applied researches. This method is able to apply in industrial production.

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