

二氧化钛纳米晶薄膜的吸收光谱和激发发射光谱

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摘要: 由 TiO₂ 反胶束溶胶制备一系列 TiO₂ 纳米晶薄膜,对膜的吸收光谱和激发发射光谱研究表明制备的膜存在有二种模式的跃迁,直接跃迁和间接跃迁。由于厚膜中存在较强的表面相互作用,厚膜的直接跃迁禁带宽与薄膜相比发生了红移。在不同陈化时间,浸渍相同次数制得的膜具有相同的直接跃迁禁带宽。除浸渍一次的膜不存在间接跃迁外,所有的膜具有相同的间接跃迁禁带宽。所有的膜具有几乎相同的发射光谱模式。

关键词: TiO₂ 纳米晶薄膜; 禁带宽; 光致发射光谱

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Absorption and Exciton Emission Spectra of Nanocrystalline Titanium Dioxide Thin Films

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Abstract: A series of TiO₂ nanocrystalline thin films were fabricated by using dip coating method from TiO₂ reverse micelle solution. The studies on absorption and exciton emission spectra showed that both the indirect and direct transition exist in these TiO₂ nanocrystalline thin films. A thick film has a red shift of direct transition bandgap than thin films due to the strong interface interaction. The films made at different aging time with same dip times have the same direct transition bandgaps. All the films have the same indirect transition bandgap, but those with one time dip have no indirect transition. All the films have almost the same patterns of photoluminescence spectra.

Key words: TiO₂ nanocrystalline thin film; bandgap; photoluminescence spectra

0 Introduction

Nanocrystalline thin films of titanium dioxide are attracting much interests due to their unique properties, such as high photocatalysis in degradation of organic compounds^[1~3], optical properties^[4~8]. K. Madhusudan Reddy etc.^[9] have studied the bandgap of bulk anatase and anatase nano-particles. They found that the bulk anatase has an indirect bandgap but nano anatase

particles have a direct bandgap. N. Serpone etc.^[10] found no size effects on the indirect bandgaps and direct bandgaps of nano-articles.

A lot of works have been done for studying on the photoluminescence of titania. A. Suisalu and co-workers^[11] observed the low temperature visible photoluminescence of nanocrystalline TiO₂ thin films grown by atomic layer deposition and the photoluminescence disappear at high temperature. Zhang etc^[12] observed

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strong visible emission bands with maxima from 577 nm to 541 nm that is governed by the recombination via the localized levels within the forbidden gap of some defect-related centers.

In this work, we fabricated a series of TiO_2 nanocrystalline thin films by using dip coating method from TiO_2 reverse micelle solution. The studies on absorption and exciton emission spectra showed that both the indirect and direct transition exist in these TiO_2 nanocrystalline thin films.

1 Experimental section

The TiO_2 reverse micelle solution was made as in ref^[13,14]. The nano titania thin films support on clean glass slide were fabricated by dip-coating in the reverse solution under different performance. A01, A05 and A10 present the films with one times, five times and ten times dip in as prepared reverse solution. B01, B05 and B10 present the films with one times, five times and ten times dip while the solution was aged for 6 h. The dip speed was $40 \text{ mm} \cdot \text{min}^{-1}$. The films were left to dry in air after a dip. Finally, the films were heated in air up to 450°C left at the maximum temperature for 30 min.

The crystallization behaviour of the films was examined by X-ray diffraction using a Rigaka D/max-3A X ray diffractometer with $\text{Cu } K\alpha$ radiation. The SEM profiles of the films were obtained using a JSM-6330F Field Emission Scanning Electron Microscope.

The optical transmittance spectra of the films were recorded using a Cary 100 UV-Vis spectrophotometer. The measuring baseline was obtained from the same glass slide used to support the films. The photoluminescence of the films were recorded using an Aminco Bowman Series 2 Luminescence Spectrometer.

2 Results and discussion

2.1 Structure and surface morphology of the films

XRD spectra of the films showed that the films were pure anatase.

Fig.1 and Fig.2 show the SEM images of the films. The diameters of the particles on different films

are different. But when we look at the images carefully, we can find that there is a basic particle with diameter about 16~20 nm on different films. The different aggregation of these basic particles forms different large particles on different films.

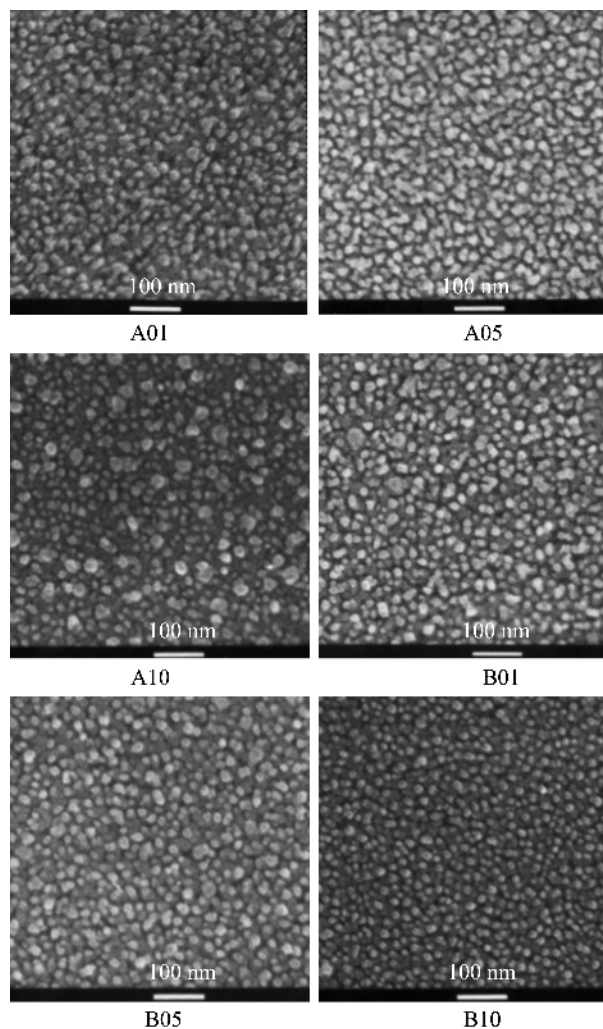


Fig.1 SEM images of the titania films

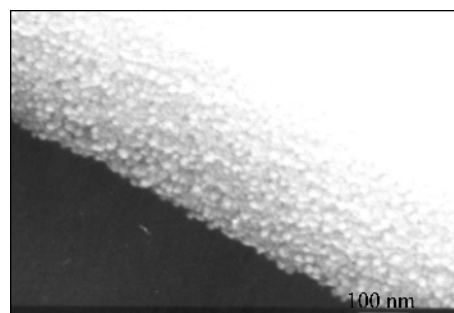


Fig.2 SEM image of cross section of film B10

2.2 Transmittance spectra and photoluminescence spectra

In general, all the films showed good transpar-

ency in visible range ($T > 80\%$). Fig.3 shows the transmittance spectra of the films. We can see from the patterns that the film with multi-dip has a red shift in the transmittance spectra.

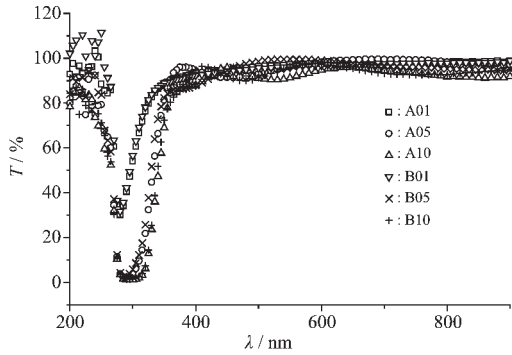


Fig.3 Transmittance spectra of the films

Fig.4 shows the comparisons of the photoluminescence spectra between different films. All the films have almost the same emission peak patterns but the intensity for different films are different. There are two wide emissions, one in the range from 307 nm (4.04 eV) to 370 nm (3.35 eV) and the other in the range from 395 nm (3.14 eV) to 445 nm (2.78 eV). It seems that the wide emission from 307 nm (4.04 eV) to 370 nm (3.35 eV) consists of two emission peaks. One is with the maximum emission at 337 nm (3.68 eV) and the other with maximum emission at 360 nm (3.44 eV). There is a sharp emission peak with maximum

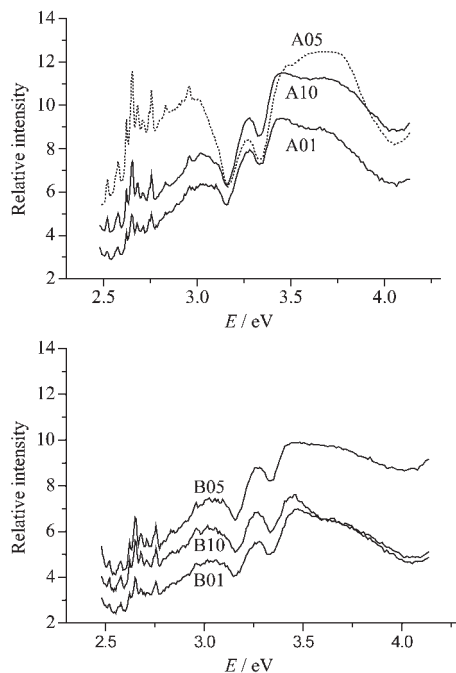


Fig.4 Photoluminescence spectra of the films

emission at 380 nm (3.26 eV). There are about 3 or 4 sharp emissions in the range from 445 nm (2.78 eV) to 500 nm (2.48 eV). Among the films made at the same aging time, the films with 5 time dips show most intensive emission. Among the films with the same dip times, the films made from as-prepared solution show more intensive emission than those from aged solution.

2.3 Bandgap of the films and the mechanisms of the photoluminescence

There are two kinds of electron transition by photon exciting, direct transition and indirect transition in semiconductor titanium dioxide. The optical absorption coefficient α near the absorption edge for direct inter band transitions is given by equation^[10]

$$\alpha h\nu = B_d (h\nu - E_g)^{1/2} \quad (1)$$

Where B_d is the absorption constant for a direct transition. Indirect interband transitions are characterized by the stronger energy dependence of the optical absorption coefficient α nearer the absorption edge than is otherwise the case for direct transition^[10].

$$\alpha h\nu = B_i (h\nu - E_g)^2 \quad (2)$$

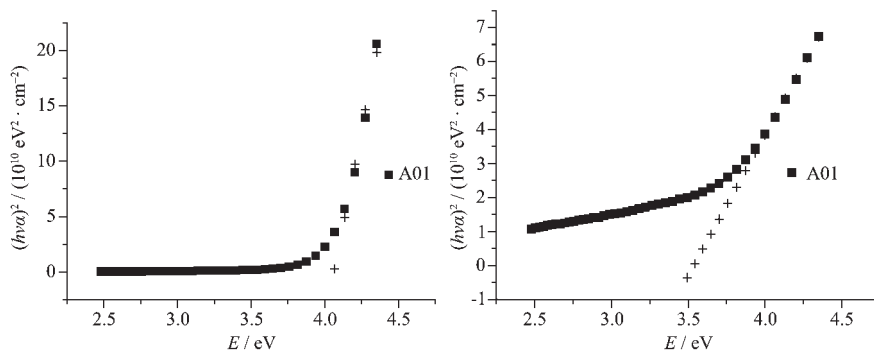
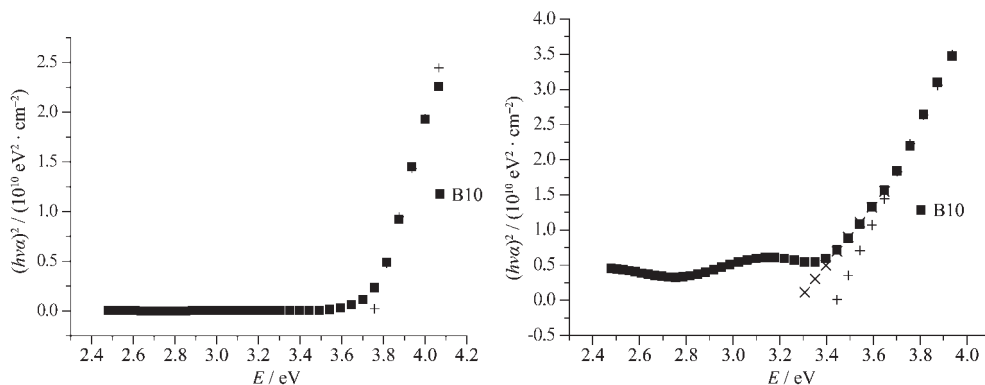
Where B_i is the absorption constant for an indirect transition.

To determine whether the absorption is caused by a direct or indirect transition, a plot of $(h\nu\alpha)^2$ versus $E\{h\nu\}$ and a plot of $(h\nu\alpha)^{1/2}$ versus $E\{h\nu\}$ were made. The plots of film A01 and film B10 were shown in Fig.5 and Fig.6. Both plots of $(h\nu\alpha)^2$ vs $E\{h\nu\}$ and $(h\nu\alpha)^{1/2}$ vs $E\{h\nu\}$ of the same film gave straight lines in different ranges of E . For example, the plot of $(h\nu\alpha)^2$ vs $E\{h\nu\}$ of film A01 gave a straight line in the range between 4.13 eV and 4.35 eV while the plot of $(h\nu\alpha)^{1/2}$ versus $E\{h\nu\}$ for the same film gave a straight line in the range between 4.00 eV and 4.35 eV. For the films with five times and ten times dips, the plots of $(h\nu\alpha)^{1/2}$ vs $E\{h\nu\}$ gave two straight lines. The film A10 has two straight lines in the plot of $(h\nu\alpha)^{1/2}$ vs $E\{h\nu\}$ with the extrapolation of 3.44 eV and 3.33 eV while $\alpha=0$ in different ranges of E . From these plots the extrapolation of all straight lines for $\alpha=0$ were calculated as indicated in Table 1.

Table 1 Thickness and extrapolation ($\alpha=0$) of the films

	A01	A05	A10	B01	B05	B10
Thickness / nm	43	238	455	47	267	486
^a Extra. 1 / eV	4.060	3.919	3.751	4.053	3.915	3.755
Range of line	4.13~4.35	4.05~4.27	3.81~4.06	4.13~4.35	4.06~4.27	3.81~4.00
^a Extra. 2 / eV	3.536	3.467	3.442	3.484	3.403	3.443
Range of line	4.00~4.35	3.70~4.00	3.70~3.93	3.94~4.35	3.64~4.20	3.70~3.94
^a Extra. 3 / eV		3.259	3.334		3.304	3.279
Range of line		3.54~3.70	3.54~3.70		3.49~3.70	3.44~3.65

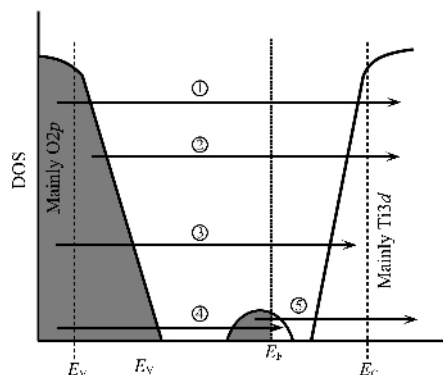
^a The Extra.1 represents extrapolation ($\alpha=0$) calculated from the plots of $(h\nu\alpha)^2$ vs $E\{h\nu\}$; The Extra.2 and Extra.3 represent extrapolations ($\alpha=0$) calculated from the plots of $(h\nu\alpha)^{1/2}$ vs $E\{h\nu\}$; The Extra.1 and Extra. 3 are the bandgaps of direct transition and indirect transition respectively and the Extra.2 is not a real bandgap.

Fig.5 Plots of $(h\nu\alpha)^2$ vs $E\{h\nu\}$ and $(h\nu\alpha)^{1/2}$ vs $E\{h\nu\}$ of film A01Fig.6 Plots of $(h\nu\alpha)^2$ vs $E\{h\nu\}$ and $(h\nu\alpha)^{1/2}$ vs $E\{h\nu\}$ of film B10

In these works, for film A01 and B01, we can assign the extrapolation of 4.05 eV and 4.053 eV to the direct transition bandgap of $\Gamma_{5'a} \rightarrow \Gamma_{1b}^{[10]}$. According to the N. Serpone's work^[10], there is no indirect transition with bandgap more than 3.2 eV. The extrapolation about 3.5 eV for all films calculated from plots of $(h\nu\alpha)^{1/2}$ versus $E\{h\nu\}$ is not a real bandgap. And this is reasonable because there is an overlap between the ranges of straight line for 3.5 eV and for direct transition. For the films with multi-dips, the bandgap of direct transition varied with the thickness

of the films. The thicker the film is, more red shift of bandgap the film has. These are because there is stronger interface interaction in the thicker films than thin films as discussed above from the SEM images of the films. These interface interaction made the octahedral unit of TiO_2 distorted that weakens the Ti-O bonding reducing splitting between bonding and nonbonding levels which give rise to the band-tails in the band structure. The energy of direct transition between band-tails is small than that between main bands, as indicated in Fig.7^[15]. From above results in

the Table 1, the thin films with one time dip has no indirect transition. Other films have indirect transition with an unvaried value about 3.3 eV. These results agreed with the results of N. Serpone's work^[10] within experimental error.



① represents the transition between main bands; ② and ③ represent the transition between band-tails

Fig.7 Schematized density of states for TiO₂ films in air and optical transitions^[15]

There have been more works of studying the photoluminescence of nano crystalline of titanium dioxide. Most works^[5,11,12,16~20] concerned with the emission in the visible range (>400 nm). Little work^[21,22] is involved in the range with wavelength $\lambda \leq 400$ nm. From above discussion and basic principle of photoluminescence, we believed that the emission band from 307 nm (4.04 eV) to 370 nm (3.35 eV) was produced from the direct transition of the films. In the range, the peak with 3.68 eV may be assigned to the direct transition between main band and 3.44 eV to the direct transition between band-tails. Sharp emission with maximum emission 380 nm (3.26 eV) may be attributed to the forbidden direct transition. This forbidden direct transition became permissive due to the localization of surface state. The emission band from 395 nm (3.14 eV) to 445 nm (2.78 eV) was produced from the indirect transition with bandgap 3.2 eV. Film A01 and B01 have no indirect transition and there is no emission in this range for these films. The sharp peaks in the range from 445 nm (2.78 eV) to 500 nm (2.48 eV) may be assigned to the transition between the valance band state and localized mid-gap state or between the localized mid-gap states and conduction band states. The localized mid-gap states

are produced from dangling bonds on the defect surface^[15].

3 Conclusion

A series of TiO₂ nano films were fabricated. The film made under different conditions has different surface morphology. All the films have direct transition with different bandgaps. Thick films with a red shift of direct transition bandgap than thin films due to the strong interface interaction. The films made at different aging time with same dip times have the same direct transition bandgaps. All the films have the same indirect transition bandgap, but those with one time dip have no indirect transition. All the films have almost the same patterns of photoluminescence spectra. Besides two wide emission bands due to the direct and indirect transition, other emission peak can also be assigned.

References:

- [1] Xagas A P, Androulaki E, Hiskia A, et al. *Thin Solid Films*, **1999**,**357**:173~178
- [2] Yu Jiaguo, Zhao Xiujian, Zhao Qingnan. *Thin Solid Films*, **2000**,**379**:7~14
- [3] Wang T M, Zheng S K, Hao W C, et al. *Surface and Coatings Technology*, **2002**,**155**:141~145
- [4] Wang Cong, Wang Tianmin, Zheng Shukai. *Physica E*, **2002**, **14**:242~248
- [5] LIU Fa-Min, WANG Tian-Min. *Applied Surface Science*, **2002**, **195**:284~290
- [6] Diana Mardare. *Materials Science and Engineering B*, **2002**, **95**:83~87
- [7] Wang Zhongchun, Helmersson Ulf, Kall Per-Olov. *Thin Solid Films*, **2002**,**405**:50~54
- [8] Bessergeneva V G, Khmelinskii I V, Pereira R J F, et al. *Vacuum*, **2002**,**64**:275~279
- [9] Reddy K M, Manorama S V, Reddy A R. *Materials Chemistry and Physics*, **2002**,**78**:239~245
- [10] Serpone N, Lawless D, Khairutdinov R. *J. Phys. Chem.*, **1995**,**99**:16646~16654
- [11] Suisalu A, Aarik J, Mandar H, et al. *Thin Solid Films*, **1998**, **336**:295~298
- [12] Zhang W F, Zhang M S, Yin Z, et al. *Appl. Phys. B*, **2000**, **70**:261~265
- [13] Hideki Sakai, Hajime Kawahara, Masuo Shimazaki, et al.

- Langmuir*, **1998**,**14**:2208~2212
- [14] Stathatos E, Tsiourvas D, Lianos P. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **1999**,**149**:49~56
- [15] Bilmes S A, Mandelbaum P. *J. Phys. Chem. B*, **2000**,**104**: 9851~9858
- [16] Hirendra Nath Ghosh, Soumyakanti Adhikari. *Langmuir*, **2001**,**17**:4129~4130
- [17] Zou Bingsuo, Xiao Liangzhi, Li Tiejin. *Appl. Phys. Lett.*, **1991**,**59**(15):1826~1828
- [18] Lin Wenyong, Pang Wenqin, Sun Jingzhi, et al. *J. Mater. Chem.*, **1999**,**9**:641~642
- [19] Jin Yunxia, Li Guanghai, Zhang Yong, et al. *J. Phys: Condensed Matter*, **2001**,**13**:L913~L918
- [20] Song Chun Feng, Lu Meng Kai, Yang Ping, et al. *Thin Solid Films*, **2002**,**413**:155~159
- [21] Castellano F N, Stipkala J M, Friedman L A, et al. *Chem. Mater*, **1994**,**6**:2123~2129
- [22] WANG Bin(王 斌), GAO Fei(高 飞), HE Bin(何 斌), et al. *Wuli Huaxue Xuebao(Acta Phys.-Chim. Sin.)*, **2003**, **19**:21~24