Research on Character of Nanocrystalline TiO_2 Film*

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Abstract: The article studied the character of nanocrystalline TiO_2 film. The spectral absorption of TiO_2 film is in positive correlation with thickness of TiO_2 film. It is a hydrate granular structure and roughness on surface of TiO_2 film that is unheating. It is a same grade granular structure and small roughness surface on TiO_2 film that is heating under air. It is a same grade granular structure and smooth surface on TiO_2 film that is heating under N_2. It is a same grade granular structure and smooth surface on TiO_2 film that is heating under air and soak in sensitivity dye for 1 hour. The transmit electric power of TiO_2 film that sintering up to 450 ℃ under air is higher than that sintering up to 530 ℃ under N_2. The screen bore diameter of printing TiO_2 film is more smaller, the transmit electric power is more larger.

Key words: TiO_2 film; TiO_2 solar cell; structure character
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Sun and wind green energy is more and more important in our life, because there are energy and environment crisis in the world. Specially, to research a solar cell that is clean, cheap and high efficiency energy products, it is a light future for scientists to do one best for that in each country.

From 1980 to now, there are more and more study in TiO_2, ZnO and Al_2O_3 solar cell by Gratzel et al[1-6]. At the same time, there were made out Gratzel's solar cell in laboratory with 10% ~ 12% photon to current conversion efficiency, cost just 1 US dollar for each peat watt and stability.

This article researched structure character of nanocrystalline TiO_2 film.

1 Materials

1.1 TiO_2 and film

The method producing TiO_2 and TiO_2 film are as follows:

(1) 100 mL $TiCl_4$ + 200 mL ethanol + 300 mL methanol + 100 mL distilled deionised water.

(2) Heated at 100 ℃, keeping 10 minute.

(3) Autoclaving at 210 ℃ for 10 hours gave particle growth up to about 20nm. Forslightly bigger particles the autoclaving temperature was 250 ℃, but this gave 20% rutile. Finally, 40% carbowax, by weight of TiO_2, was added after water had been partly evaporated to yield a viscous sol. The sol was then deposited on SnO_2 layer of 2 μm, supported on glass. Part of them heating under air for 30 minutes at 450 ℃ and under N_2 for 30 minutes at 530 ℃ gave electrodes 16 ~ 25 μm thick with a porous, nanocrystalline morphology.

1.2 $[RuL_2(NCS)_2]\cdot 2H_2O$ sensitivity dye

cis-Dicyanobis Ru2 + trihydrate was synthesized by dissolving 235 mg of KCN in 10 mL of H_2O and transferring it into a three neck flask containing 30 mL of DMF. Then, 500 mg of RuL_2Cl_2 (L_2 = 2,2'-bipyridyl-4, 4'-dicarboxylic) was introduced into the above solution. The reaction mixture was then heated to reflux under N_2 for 5 hours. After the time, the reaction mixture was allowed to cool and then filtered through a glass frit. The filtrate was evaporated to dryness on a rotatory evaporator, and the resulting solid was dissolved in H_2O at pH 10. Upon addition of dilute $HClO_4$ to the above solution, most of the complex salt at pH 2 ~ 3. The orange solid was isolated by suction filtration, washed well with H_2O, ethyl alcohol, and anhydrous diethylether, and air dried for 1 hour.

1.3 Electrolyte

Electrolyte had been complexed with 0.5 mol LiI + 0.04 mol I_2 + [60% propylene carbonate and 40% acetonitrile(volume)].

2 Test and analysis

2.1 Test spectral absorption of TiO_2 film

Test spectral absorption with different TiO_2 film by Hicth UV-340 spectrometer with 0.1 nm spectrum resolution in band 400 ~ 850 nm. The part of test results are shown in Fig.1.

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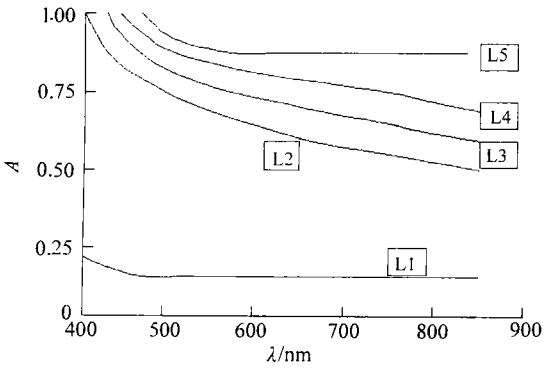

Fig.1 The spectral absorption of TiO_2 films

L1: Printing TiO_2 sol over SnO_2 glass, the screen bore diameter is 15 μm, heating under air for 30 minutes at 530 ℃, thickness of TiO_2 film is 2μm.

L2: Printing TiO_2 sol over SnO_2 glass with thickness of TiO_2 film is 20μm, the screen bore diameter is 15μm.

L3: Printing TiO_2 sol over SnO_2 glass, the screen bore diameter is 30 μm, heating under air for 30 minutes at 530 ℃, then, soak in red Chinese tea for 1 hour. Thickness of TiO_2 film is 20μm.

L4: Printing TiO_2 sol over SnO_2 glass, the screen bore is 30 μm. Heating under air for 30 minutes at 530 ℃. Then soak in sensitivity dye for 1 hour. Thickness of TiO_2 film is 20 μm.

L5: Printing TiO_2 sol over SnO_2 glass, the screen bore diameter is 30 μm. Heating under air for 30 minutes at 530 ℃. Then soak in sensitivity dye for 1 hour. Thickness of TiO_2 film is 25 μm.

2.2 Field emission scanning electron microscope (ESEM) analysis

TiO_2 film analysis by ESEM used for character analysis of structure, roughness and thickness on surface of TiO_2 film. A part of results are shown in Fig.2,3.

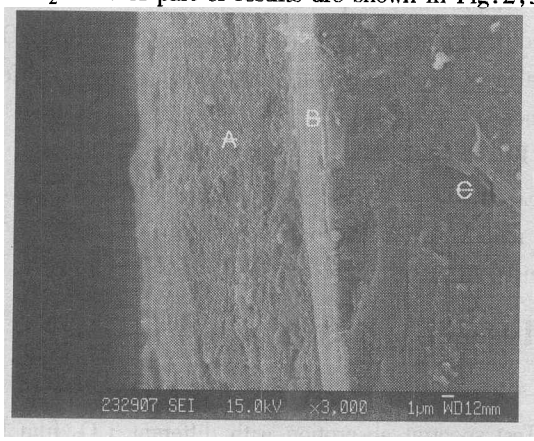

Fig.2 Thickness ESEM image of TiO_2 film

A: TiO_2 film (thickness 16 ~ 20 μm);

B: SnO_2 film (thickness 2 μm);

C: Glass.

ESEM analysis by JSM-633OF in analysis center of Sun Yat-sen University. Resolution is 1.5 nm

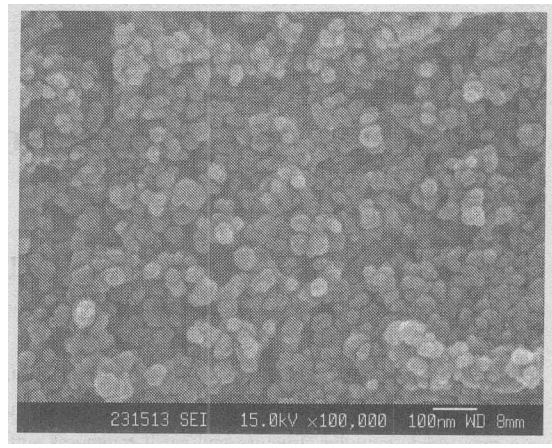

Fig.3 ESEM image on surface of TiO_2 film printing TiO_2 sol over SnO_2 glass

The screen bore diameter is 30μm.

Heating under N_2 for 30 minutes at 450 ℃.

The diameter of TiO_2 is 20 ~ 40 nm, ESEM analysis by Japanese JSM-633OF in analysis center of Sun Yat-sen University.

2.3 Atom forcemeter (AFM) analysis

TiO_2 film was analysed by AFM for character analysis of structure and roughness on surface of TiO_2 film. The results are showed in Fig.4.

2.4 Photocurrent action

The nanopolycrystalline photovoltaic cell has been made with TiO_2 film, sensitivity dye, LiI electrolyte, Pt, and SnO_2 glass, then, test photocurrent action character under 60 W/cm^2 solar emission. The part of results list in Tab.1.

3 Results and Discussion

3.1 Spectral absorption character

Spectral absorption is related with thickness of TiO_2 film (Fig. 1). TiO_2 film is thicker, the absorption is larger. For example, when the thickness of TiO_2 film is 2 μm, the average value of spectral absorption is 15% (Fig. 1, L1). When thickness of TiO_2 film is 25 μm, the average value of spectral absorption is over 95% (Fig.1, L5). The spectral absorption of TiO_2 film, its printing screen bore diameter is 20 μm, it is higher than that when its diameter is 30 μm (Fig.1, L3 compare with L4, L5).

3.2 Structure character

Thickness of TiO_2 film is between 16 ~ 25 μm by screen bore diameter of printing is 30 μm. Thickness of SnO_2 film is 2 μm (Fig. 2). When the TiO_2 film was heated under N_2 for 30 minutes at 450 ℃, there were granular structure, the diameter of TiO_2 was between 25 ~ 40 nm, smoother on surface of TiO_2 film (Fig.3).

Tab.1 Nanopolycrystalline photovoltaic cell photocurrent action character

Sample No.	1	2	3	4	9	20	25	26	27	28
Screen bore diameter/μm	30	30	30	30	30	30	30	15	30	59
Heating temperature of TiO_2 film/℃	450	450	450	450	530	530	530	530	530	530
Electric power/(mW·cm^{-2})	0.952	0.645	0.482	0.216	0.253	0.413	0.590	0.390	0.325	0.180

All thickness of TiO_2 film is 20 μm.

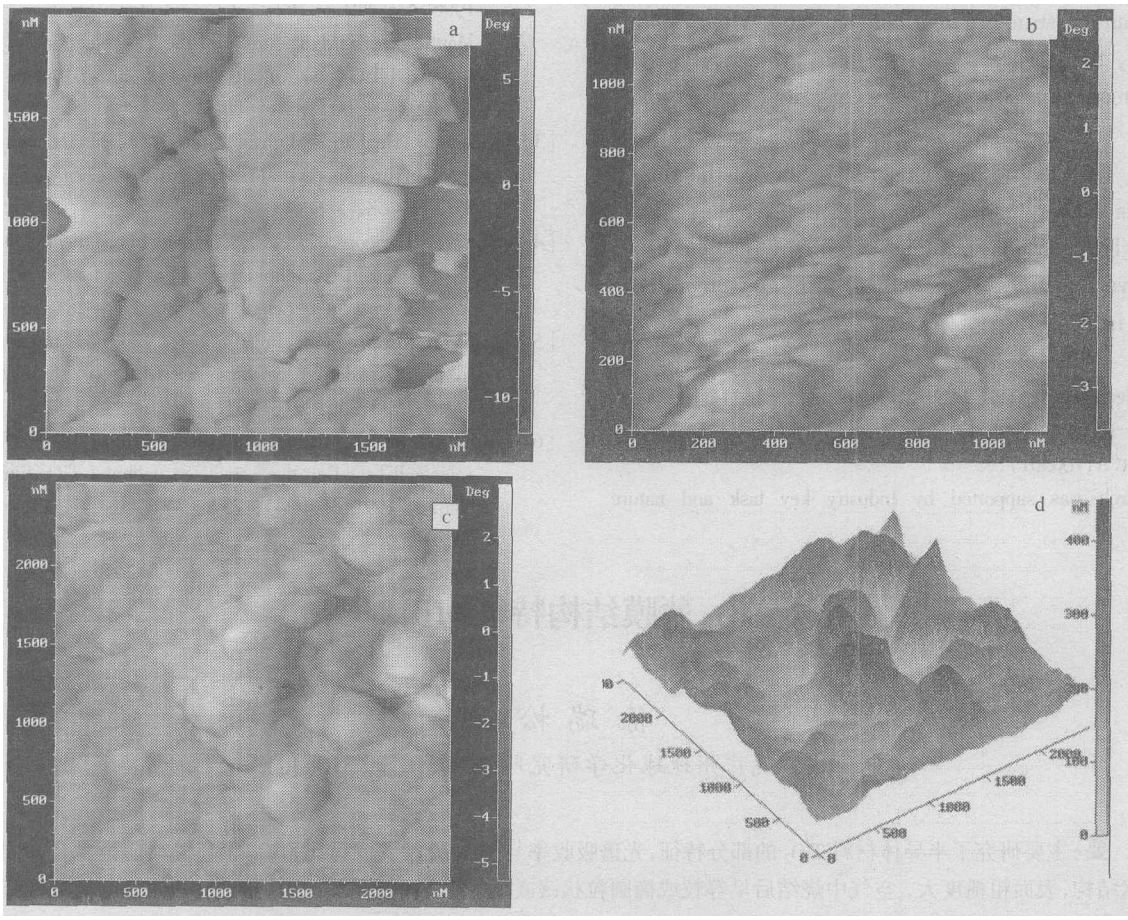

Fig.4 AFM image on surface of TiO_2 film

Printing TiO_2 sol over SnO_2 glass, the screen bore diameter is 30 μm.

Heating under air for 30 minutes at 450 ℃.

a is unheating. b is heating. c is soak in sensitivity dye for 1 hour after heating. d is 3D image of c.

Analysis by Russian NT-MDT AFM in vacuum laboratory of Physical Institute, Chinese Academy of Sciences.

Unheating surface of TiO_2 film is a hydrate granular structure and roughness(Fig.4,a). The diameter of TiO_2 is between 50 ~ 300 nm. The height on surface of TiO_2 film is larger than 800 nm that is unheating(Fig.4,a). When the TiO_2 film was heated under air for 30 minutes at 450 ℃, there are granular structure, the diameter of TiO_2 is between 30 ~ 180 nm, smoother on surface of TiO_2 film. The height on surface of TiO_2 film is between 300 ~ 500 nm (Fig.4, b). When the TiO_2 film was heated under air for 30 minutes at 450 ℃ and soak in sensitivity dye for 1 hour, there are granular structure, the diameter of TiO_2 is between 30 ~ 200 nm, smooth on surface of TiO_2 film. The height on surface of TiO_2 film is between 300 ~ 400 nm (Fig.4,c,d).

3.3 Photocurreut action character

The electric power of sample 1, 2, 3, 4 that is heating at 450 ℃ (mean value is 0.559 mW/cm^2) is higher than sample 9, 20, 25, 26, 27 and 28 that is heating at 530 ℃ (mean value is 0.342 mW/cm^2, Tab.1). Under same condition, the electric power of sample 26 that printing screen bore diameter is 15 μm, is over 2 times higher than sample 28 that printing screen bore diameter is 59 μm (Tab.1).

4 Conclusion

(1) The TiO_2 film is thicker, the spectral absorption is stronger in band 400 ~ 850 nm.

(2) Unheating surface of TiO_2 film is hydrate granular structure and more roughness. Heating surface of TiO_2 film display granular structure and smooth. After heating and soak in sensitivity dye, the surface of TiO_2 film is granular structure and more smooth. When Heating under N_2, the surface of TiO_2 is more average, Pellet of TiO_2 is more fine, and surface of TiO_2 film is more smooth.

(3) The electric power that TiO_2 film was heating at 450 ℃ is higher than heating at 530 ℃. The electric power of TiO_2 film that printing screen bore diameter is 15 μm is over 2 times higher than printing screen bore diameter is 59 μm.

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TiO_2 薄膜结构特征初探

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摘 要:主要研究了半导体材料 TiO_2 的部分特征,光谱吸收率与 TiO_2 膜厚度成正比,TiO_2 膜在烧结前呈水合物团块状结构,表面粗糙度大,空气中烧结后呈等粒或椭圆粒状镶嵌结构,表面粗糙度比未烧的小,在抽真空加氮气烧结后成等粒状结构,表面较光滑,在空气中烧结的 TiO_2 膜放至光敏染料中泡 1 h 后呈等粒状结构,表面较光滑。从 TiO_2 光电池器件输出电功率来看,TiO_2 膜在空气中烧至 450 ℃时的电输出的功率比在氮气中烧至 530 ℃的高,印刷 TiO_2 膜的丝网目数为 500 目时,电输出功率较佳。

关键词:TiO_2 光电池;TiO_2 薄膜;结构特征

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