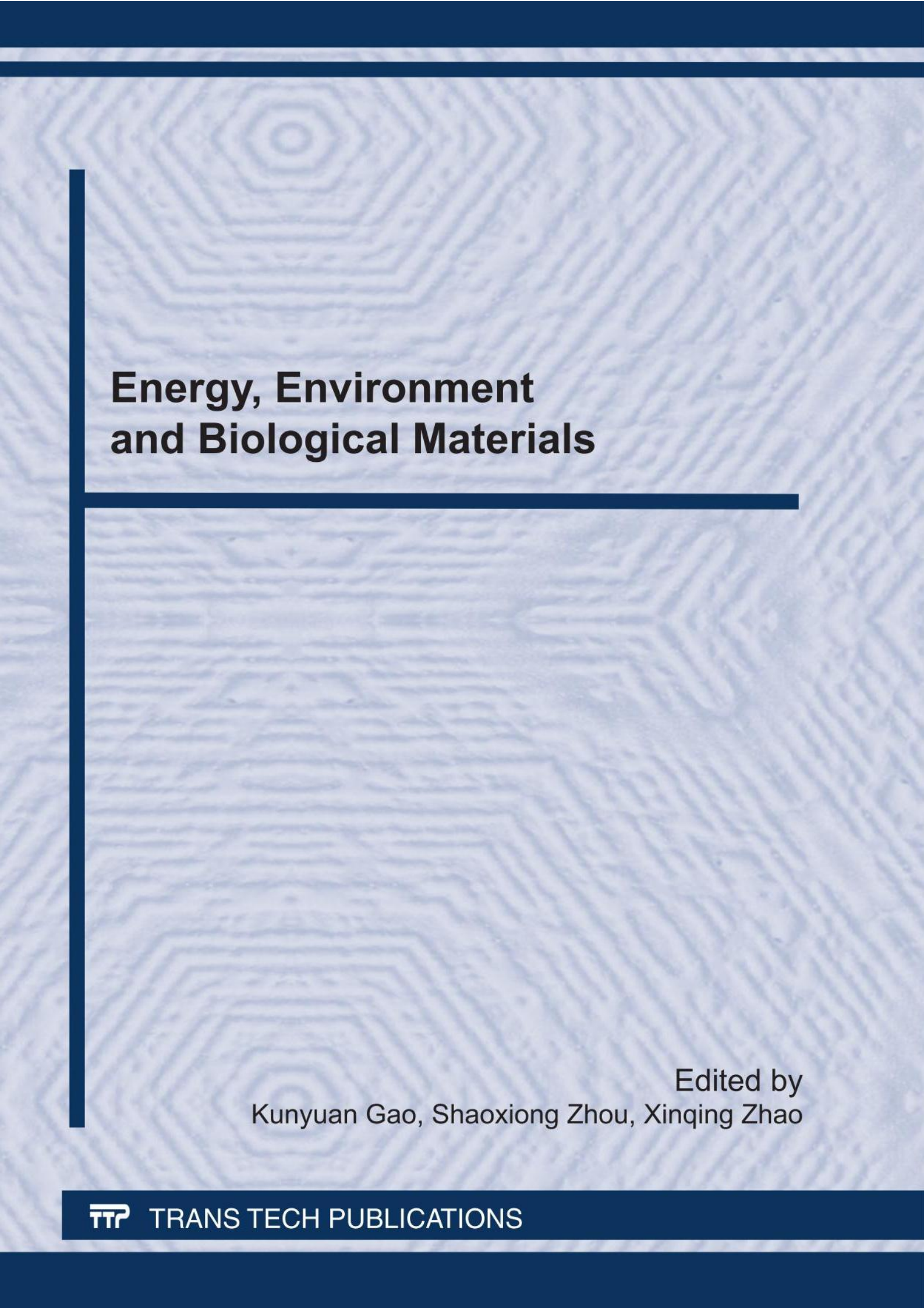




Energy, Environment and Biological Materials

Edited by
Kunyuan Gao, Shaoxiong Zhou, Xinqing Zhao

Energy, Environment and Biological Materials

Edited by
Kunyuan Gao
Shaoxiong Zhou
Xinqing Zhao

Energy, Environment and Biological Materials

Selected, peer reviewed papers from
11th IUMRS International Conference in Asia
(IUMRS-ICA 2010),
25-28 September 2010,
Qingdao, China

Edited by:

Kunyuan Gao, Shaoxiong Zhou and Xinqing Zhao



Copyright © 2011 Trans Tech Publications Ltd, Switzerland

All rights reserved. No part of the contents of this publication may be reproduced or transmitted in any form or by any means without the written permission of the publisher.

Trans Tech Publications Ltd
Kreuzstrasse 10
CH-8635 Durnten-Zurich
Switzerland
<http://www.ttp.net>

Volume 685 of
Materials Science Forum
ISSN 0255-5476

Full text available online at <http://www.scientific.net>

Distributed worldwide by

Trans Tech Publications Ltd
Kreuzstrasse 10
CH-8635 Durnten-Zurich
Switzerland

Fax: +41 (44) 922 10 33
e-mail: sales@ttp.net

and in the Americas by

Trans Tech Publications Inc.
PO Box 699, May Street
Enfield, NH 03748
USA

Phone: +1 (603) 632-7377
Fax: +1 (603) 632-5611
e-mail: sales-usa@ttp.net

Preface

This is the proceedings of the selected papers presented at 11th IUMRS International Conference in Asia (IUMRS-ICA2010) held in Qingdao, China, Sept. 25-28, 2010.

The IUMRS International Conference in Asia (IUMRS-ICA) is one of the most important serial conferences of the International Union of Materials Research Societies (IUMRS) and is organized by all of the Materials Research Societies in the Asian area. The first IUMRS-ICA was organized by C-MRS in September 1993 on a ship in the Yangtze River, and has been organized subsequently by MRS-T, MRS-K, MRS-J, MRS-India, and MRS-Singapore. IUMRS-ICA provides the opportunity for scientists, engineers, and students from not only Asia but around the world to exchange their recent achievements in the field of materials research and development. IUMRS-ICA 2010 was organized by C-MRS and co-organized by MRS-T and MRS-J.

IUMRS-ICA 2010 had 21 Symposia covering six fields of Energy and environmental materials; Advanced structural materials; Functional and electronic materials; Nano-scale and amorphous materials; Health and biological materials; and Materials modeling, simulation and characterization. Nearly 1400 participants from 20 countries and areas attended the conference, and the conference organizers received about 1000 technical papers. By recommendation of symposium organizers and after peer reviewing nearly 500 papers are published in the present proceedings, which divided into five volumes of

Part 1: Energy, environmental and bio-medical Materials

Part 2: Advanced Structural Materials

Part 3: Functional and Electronic Materials

Part 4: Nano-scale and Amorphous Materials

Part 5: Materials Modeling, Simulation, and Characterization

This is the volume for Part 1 including the papers selected from Symposium A:solar cells, Symposium D:eco-materials and technology on climate change and Symposium S:bio-medical Materials.

The editors would like to give special thank to the symposium organizers and graduate students Meiling Wu, Liwu Jiang, Dongliang Cui, Xiaoying Xie and Fulin Li et al. from Beihang University for their hard work of compilation and typesetting for each paper in this volume.

Editors

IUMRS-ICA 2010

11th IUMRS International Conference in Asia

September 25-28, 2010, Qingdao, China

Organized by

Chinese Materials Research Society(C-MRS)

International Union of Materials Research Societies(IUMRS)

Co-organized by

Materials Research Society-Taiwan (MRS-T)

Materials Research Society- Japan (MRS-J)

Sponsored by

Government of Qingdao City, Shandong Province, China

Supported by

Ministry of Science and Technology of China

China Association for Science and Technology

National Natural Science Foundation of China

Chinese Academy of Sciences

Chinese Academy of Engineering

Table of Contents

Preface, Organizing Committees and Sponsors

Solar Cells

A Novel Counter Electrode Based on Hierarchical Porous Carbon for Dye-Sensitized Solar Cells

G.Q. Wang, W. Xing and S.P. Zhuo 1

Aluminum-Doped Zinc Oxide as Transparent Electrode Materials

Y.L. Zhang, X.P. Zhang, R.Q. Tan, Y. Yang, J.H. Zhao, W.Y. Wang, P. Cui and W.J. Song 6

Study on Determination of I-V Curve of Dye-Sensitized Solar Cell

H.M. Tian, T. Yu and Z.G. Zou 13

Effect of the Residual Template on Surface Photoelectric Characteristics of Structurally-Ordered Macroporous Nanocrystalline TiO_2

S.L. Wei, K.Y. Li, W.Y. Yang, C.M. Wang and J. Zhang 20

A Simple Texturization Approach for Mono-Crystalline Silicon Solar Cell with Low TMAH Concentration Solution

W.Y. Ou, Y. Zhang, H.L. Li, L. Zhao, C.L. Zhou, H.W. Diao, M. Liu, W.M. Lu, J. Zhang and W.J. Wang 26

Effects of IPA on Texturing Process for Mono-Crystalline Silicon Solar Cell in TMAH Solution

W.Y. Ou, Y. Zhang, H.L. Li, L. Zhao, C.L. Zhou, H.W. Diao, M. Liu, W.M. Lu, J. Zhang and W.J. Wang 31

Efficient Hybrid Infrared Solar Cells Based on P3HT and PbSe Nanocrystal Quantum Dots

Z.N. Tan, W.Q. Zhang, D.P. Qian, H. Zheng, S.Q. Xiao, Y.P. Yang, T. Zhu and J. Xu 38

Enhancing the Performance of Dye-Sensitized Solar Cells by Incorporating Mesoporous Carbon in Polymer Gel Electrolyte

G.Q. Wang, L. Wang and S.P. Zhuo 44

Excellent Surface Passivation by Silicon Dioxide Grown with a Electrochemical Method

J. Zhang, W.M. Lu, C.L. Zhou, Z.L. Wen, L. Zhao, H.L. Li, H.W. Diao, Y. Zhang and W.J. Wang 48

Gelation of Ionic Liquid-Based Electrolyte with Ordered Mesoporous Silica Particles for Quasi-Solid-State Dye-Sensitized Solar Cells

G.Q. Wang, L. Wang, W. Xing and S.P. Zhuo 55

Graded Buffer Layer Effect on Performance of the Amorphous Silicon Thin Film Solar Cells

S.Y. Lien, M.J. Yang, Y.S. Lin, C.F. Chen, P.H. Lin, C.H. Hsu, P.C. Huang and Y.M. Shen 60

Hydrothermal Growth of ZnO Nanowires on Patterned Seed Layer

W.G. Zhao, Q. Zhang and Z.Q. Ma 65

Improved Gel Electrolyte by Layered α -Zirconium Phosphate for Quasi-Solid-State Dye-Sensitized Solar Cells

L. Han, N. Wang, H.C. He, D.T. Kong and H.J. Chen 71

Influence of Polymer Concentration on Polysaccharide Electrolyte for Quasi-Solid-State Dye-Sensitized Solar Cell

Y. Yang, X.Y. Guo and X.Z. Zhao 76

Light Trapping in Dye Sensitized Solar Cells with Length-Modulated TiO_2 Nanotubes

C. Shen, L. Shen, J. Yang, J.W. Shi, F. Xu and Z.Q. Ma 82

Lower-Temperature Preparation and Photoelectrochemical Properties of Anatase TiO_2 Sol

J. Deng, J. Tao, X.L. Liu and T. Wu 87

Mechanism of Blue Shift of Optical Band Gap in Aluminum-Doped ZnO Thin Films with Blend Bond

L. Shen, C. Shen, J. Yang, F. Xu and Z.Q. Ma 98

Preparation and Characterization of $\text{Cu}_2\text{ZnSnSe}_4$ Thin Films by Selenization of Electrodeposited Metal Precursors

J. Li, Z.W. Zhang, Y. Ou, W.F. Liu, G.S. Jiang and C.F. Zhu 105

Properties of Fe Doped Amorphous Carbon Thin Films for Photovoltaic Solar Cell Applications

X.Y. Tan, X.Z. Zhang, C.H. Wan and X.L. Gao 110

Relationship between Microstructure and Photoelectron Behaviors of CdTe/Ligand Self-Assembly Quantum Dots	
W.Y. Yang, K.Y. Li, S.L. Wei, G.J. Song and J. Zhang	114
Solar Grade Silicon Materials and Poly-Silicon Solar Cell	
Y.C. Gao, B.T. Zhao and W.X. Gao	119
Synthesis of Colloidal Carbon Spheres by Hydrothermal Carbonization of Glucose at Different Initial pH	
G.H. Jiang, X.Q. Xu and G. Xu	123
The Application of Simulation and Optimization in the Growth of High-Purity Silicon Thin Film on Low-Purity Silicon Substrate by Liquid Phase Epitaxial	
Y.C. Gao, B.T. Zhao and W.X. Gao	130
The Effect of Target to Substrate Distance on the Properties of HAZO Films Deposited by Magnetron Sputtering	
W.M. Lu, J. Zhang, H.W. Diao, L. Zhao and W.J. Wang	134
The Study of Flower-Shaped Structure Dislocation in 4 Inch <100> Germanium Single Crystal	
M.M. Li, X.P. Su, D.S. Feng, J.L. Zuo, N. Li and X.W. Wang	141
Thermal Stability of Aluminum Doped Zinc Oxide Thin Films	
J.H. Huang, R.Q. Tan, J. Li, Y.L. Zhang, Y. Yang and W.J. Song	147
A Research on Energy-Saving and Environmental Impacts of Primary Magnesium and Magnesium Alloy Production in China	
F. Gao, Z.R. Nie, Z.H. Wang, X.Z. Gong and T.Y. Zuo	152
Application of <i>Mikania micrantha</i> as an Additive of High Strength Eco-Materials	
Y.P. Huang, C.C. Chien, Y.J. Liou, W.J. Huang and T.Y. Chang	161
Application of Rice Husk Charcoal on Remediation of Acid Soil	
C.C. Chien, Y.P. Huang, J.G. Sah, W.J. Cheng, R.Y. Chang and Y.S. Lu	169
CO₂ Emissions due to Cement Manufacture	
C. Li, X.Z. Gong, S.P. Cui, Z.H. Wang, Y. Zheng and B.C. Chi	181
Components of <i>Cunninghamia lanceolata</i> Heartwood Extracts	
J. Wang, J. Li and S.J. Li	188
Criteria for Evaluation for Eco-Material and the Case Study in Japan	
M. Nara	195
Experimental Research on Ultrafine Coal Powder for Methane Adsorption	
Z.Z. Zhang, S. Zhou and B.T. Wang	202
Influence of Particle Size Distribution of Fly Ash on Compressive Strength and Durability of Portland Cement Concrete	
J.P. Zhu, Q.L. Guo, D.X. Li and C.J. Li	211
Investigation of <i>Mikania micrantha</i> Charcoal Applied on Cultural Media	
Y.P. Huang, C.W. Peng, Y.H. Huang, T.R. Tsai, W.R. Kuo and H.C. Lin	216
Matrix-Based Model of the Carbon Footprint Analysis for Thermal Power Generation in China	
B.X. Sun, X.Z. Gong, Y. Liu, W.J. Chen and Z.H. Wang	230
PILCs as Water-Transmitting Material and Application in Planting Trees in Drought Areas	
Z.Z. Zhang, B.T. Wang and S. Zhou	239
The Adsorption Performance Study of Acid Leaching Residue of Asbestos Tailings	
J.T. Chen, Y.X. Han, S.F. Ding and S.L. Zheng	246
Process Behavior and Application of Dynamic Self-Adjusting Water-Transferring Composite Coat	
Z.Z. Zhang and H.M. Du	253
Reaction Mechanism between Zn²⁺ and Diatomite in Preparation of Zn²⁺/Diatomite Antibacterial Agent	
N. Liang, H. Ding, Y.T. Hu and B.K. Wang	260
Research on the SDS + Castor Oil Aqueous Solution Used as Methane Absorption and Gas Explosion Suppression Material	
Z.Z. Zhang, H.M. Xu and N. Gu	264
Structural Characteristics of the Fly Ash Wrapped by the Super Absorbent Resin among the Plant Fiber and the Application Research on the Complex	
J. Zhao, P.Y. Deng and S.C. Chen	272

Subjects on Fatigue Crack Generation in High Strength Alloys for Long-Life Design O. Umezawa and S. Morooka	278
Synthesis and Characterization of a Rosin Gemini Surfactant Z.J. Chen, S.J. Li, B. Tian, T. Liang and Y. Jin	285
Synthesis of Quaternary Ammonium Salt from Rosin and its Inhibition to some Wood Decay Fungi Y. Jin, S.J. Li, T. Liang and Z.J. Chen	291
Synthesis of Zeolite 4A from Kaolin and Bauxite by Alkaline Fusion at Low Temperature Y.L. Zhu, Z.H. Chang, J. Pang and C.J. Xiong	298
Effect of Small Amount of Zn Additions on the Magnetocaloric Properties of $Gd_5Si_2Ge_2$ Alloy X.Z. Wang, J. Xiang, Z. Zeng, X.H. Hu, X.L. Hou and H. Xu	307
The Influence of the Purity of Gd on the Magnetocaloric Effect in $Gd_5Si_{2-x}Ge_{2-x}Zn_{2x}$ Alloys Z. Zeng, X.Z. Wang, J. Huang, J. Xiang and X.L. Hou	311
The Performance Study of Aviation Fuel Added with Alcohols Y.L. Zhu, Z.Y. Meng, Z.H. Chang and C.J. Xiong	316
Bio-Medical Materials	
Biosynthesis of Carboxymethylated Bacterial Cellulose Composite for Wound Dressing J.W. Yu, X.L. Liu, C.S. Liu and D.P. Sun	322
Biotribology Behavior of Ultra-High Molecular Weight Polyethylene against Carbon/Carbon Composites Used for Hip Joint Replacement L.L. Zhang, H.J. Li, K.Z. Li, L.J. Guo, W.F. Cao and X.T. Shen	327
Degradation Experiments and Modeling of PLGA Blend and Gradient Films H.Z. Liu, M. Qi, X.H. Zhu and Z.Y. Wei	331
Effect of Hydroxyapatite Matrix on the Growth of Carbon Nanotubes via a CVD System X.Y. Lu, B.H. Wu, Y.J. Liu, T. Qiu and J. Weng	335
High Temperature Stability of SiC/Ti Interface T.W.L. Ngai, C.X. Hu, W. Zheng, H. Xie and Y.Y. Li	340
Inhibition of Taq DNA Polymerase and DNA Exonuclease <i>ExoIII</i> by an Aqueous Nanoparticle Suspension of a Bis-Methanophosphonate Fullerene F. Kang and G.G. Song	345
Inhibitory Effect of Hydroxyapatite Nanoparticles on K562 Cells H.L. Dai, P. Chen, Y.C. Han, X.Y. Wang and S.P. Li	352
Mechanical Properties and Microstructure of Short Carbon Fiber Reinforced Hydroxyapatite Bio-Composite X.G. Wang, W.L. Gu and Z.W. Niu	357
Modification of Pearl Surface Microstructure by Rare Earth Cerium Induced Growing W.L. Shi and X.Y. Ma	362
Preparation and Characterization of Zn-Containing Hydroxyapatite/TiO_2 Composite Coatings on Ti Alloys M. Qi, D.Y. Yang, J.Y. Zhang and H.J. Ai	367
Strontium-Borosilicate-Co-Effects to Stimulate Bone Regeneration Y.H. Shen, K.B. Zhang, H.B. Pan, W.W. Lu, Z.M. Zheng, D.P. Wang, L.F. Deng, N. Zhou and W.H. Huang	371
Mechanism of High Fracture Strength of Bone B. Chen, D.G. Yin, Q. Yuan, J. Luo and J.H. Fan	379
Study on the Cytotoxicity <i>In Vitro</i> of Composite Materials Based on Poly(L-Lactide-Co-Glycolide) and Bioactive Glass Z.H. Zhou, Y.Y. Gao, Q.F. Yi, Q.Q. Liu and L.H. Liu	384
Synthesis, Microstructure and Properties of Poly(L-Lactic Acid-Co-α-Alanine) Obtained by Direct Melting Copolymerization L. Liu, X.W. Chen, P. Wang, Z.Y. Wei, C.Y. Liu and M. Qi	390
Tetracycline Double Labelling Tracing Investigation for <i>In Vivo</i> Osteogenetic Course of PDLLA/HA Composite X.Y. Wang, X.Z. Shan, Y.C. Han and S.P. Li	394

A novel counter electrode based on hierarchical porous carbon for dye-sensitized solar cells

Guiqiang Wang^a, Wei Xing, Shuping Zhuo

College of Chemical Engineering, Shandong University of Technology, Zibo 255049 China

^awgqiang123@163.com

Keywords: Counter electrode; Hierarchical porous carbon; Dye-sensitized solar cells.

Abstract. Hierarchical porous carbons (HPC) were synthesized by a combination of self-assembly and chemical activation method. A mesoporous carbon with large-size pore was used as raw materials. N₂ sorption measurement indicated that plenty of micropores generated within the mesopore wall in the mesoporous carbon during KOH activation. Electrochemical impedance spectroscopy measurement demonstrated a high electrocatalytic activity of HPC electrode for triiodide reduction. The overall conversion efficiency of dye-sensitized solar cells with HPC counter electrode was 6.48%, which is similar to that of the device with conventional Pt counter electrode.

Introduction

Dye-sensitized solar cells (DSCs) have attracted much attention and have been considered as an alternative to a conventional photovoltaic device due to their low production cost, facile fabrication process and high-energy conversion efficiency [1-3]. Simply, a DSCs consists of a dye-sensitized nanocrystalline TiO₂ photoanode, an electrolyte containing redox couple of iodide/triiodide and a counter electrode. Under illumination, a net direct current would pass from the photoelectrode to the counter electrode within DSCs, and then from the counter electrode to the photoelectrode in the external circuit of this device, finally form a circuit. The counter electrode of DSCs serves to transfer electrons from external circuit to the electrolyte. Up to now, a thin layer of Pt deposited on transparent conducting substrates has been frequently used as the counter electrode in DSCs for its high electrocatalytic activity for triiodide reduction [4,5]. However, Pt is expensive and shows limited stability in corrosive electrolyte containing triiodide [6]. Therefore, it is necessary to seek a low-cost alternative material for the counter electrode with chemical inert, high conductivity and good electrocatalytic activity for triiodide reduction.

In recent years, conducting polymers [7,8] and carbon materials employed as the cost-effective alternatives to Pt in DSCs have been extensively investigated. Among these materials, carbonaceous materials are quite attractive due to their high electronic conductivity, corrosion resistance to iodine, high electrocatalytic activity for triiodide reduction and low cost. Several different carbonaceous materials, such as carbon black [9], carbon nanotube [10], hard carbon sphere [11] and mesoporous carbon [12,13], have been used as the counter electrode in DSCs. According to the reports, the carbon material with high surface area and accessible porous structure is more suitable to be used as the counter electrode materials. Therefore, we synthesized a hierarchical porous carbon (HPC) contained large quantity both of micropores and mesopores, and prepared the HPC counter electrode for DSCs. The overall conversion efficiency of DSCs with HPC counter electrode was 6.48%, which is similar to that of the cell with Pt counter electrode.

Experimental

The preparation of HPC is illustrated in Fig. 1, which comprises of MC preparation by self-assembly and the post activation by KOH.

MC was prepared by the self-assembly of the template agent and carbon precursor, and followed by carbonization [12]. The as-prepared MC was ground into the fine powder by using a planetary ball mill. 3g MC powder and 8 ml acetone was added into a solution of KOH (the mass ratio of KOH to

MC is 4:1). The above mixture was stirred at 100 °C in order to evaporate the acetone and water. When the mixture turned into muddy, it was transferred into a tube furnace for activation in N₂ atmosphere at 800 °C. Obtained product was washed with excess distilled water under vigorous stirring till the pH of the mixture was about 7. After filtrating and drying, HPC was obtained.

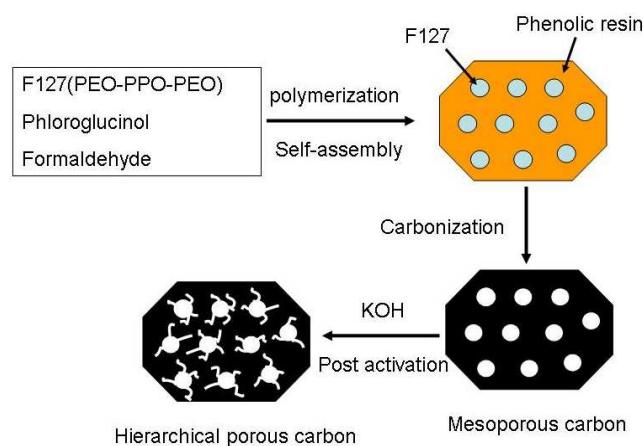


Fig. 1 Preparation strategy of HPC

HPC counter electrodes were fabricated by pasting HPC on fluorine-doped tin oxide (FTO) conducting glass, and then sintered at 400°C for 15 min. HPC paste was obtained by grinding 150 mg the mixture of HPC, 7 ml of n-butanol and 0.1 ml of tetrabutyl titanate in a mortar.

Nanocrystalline TiO₂ electrodes with the thickness of 12 µm were prepared by depositing TiO₂ colloidal paste on FTO glass and then sintered at 450 °C for 30 min in the air. After cooling to 80 °C, the TiO₂ electrodes were immersed into the solution of N3 dye (RuL₂(SCN)₂, L=2,2'-bipyridyl-4,4'-dicarboxylic acid) in ethanol for 12 h at room temperature. A DSC was fabricated by clamping a dye-sensitized TiO₂ electrode, a drop of electrolyte and a counter electrode with two clips. The electrolyte was prepared by dissolving 0.3 M 1-methyl-3-propylimidazolium iodide, 0.05 M iodine, 0.3 M LiI and 0.2 M 4-tert-butylpyridine in 3-methoxypropionitrile.

Micromeritics ASAP 2020 instrument was employed to characterize the surface area and the pore structure of the carbon samples by N₂ sorption at 77 K. Electrochemical impedance spectroscopy was conducted on a SOLARTRON SI 1287 electrochemical interface equipped with a SOLARTRON 1255B frequency response analyzer. The photovoltaic performances of DSCs were measured by a PAR potentiostat (model 273) under irradiation of 500 W Xe lamp at the light density of 100 mW cm⁻².

Results and discussion

The N₂ adsorption-desorption isotherm of MC and HPC are shown in Fig. 2. As shown in Fig. 2, the N₂ adsorption-desorption isotherm of HPC is typical of type IV and displays a pronounced hysteresis loop at medium relative pressure, which indicates that the mesopores were preserved during the KOH activation. On the other hand, in the relative pressure below 0.1, the adsorption amount of HPC is higher than that of pristine MC, which confirms the formation of micropores in large quantities. Accordingly, the as-prepared HPC contain abundant amounts of both the micropores and the mesopores. The pore structural parameters of HPC and pristine MC are summarized in Table 1. The micropore surface area, mesopore surface area and the total pore volume of HPC is higher than that of pristine MC. The increase in the mesopore area may be due to the micropore collapse caused by the over-activation. It is expected that several adjacent micropores collapsed and thus formed the mesopore.

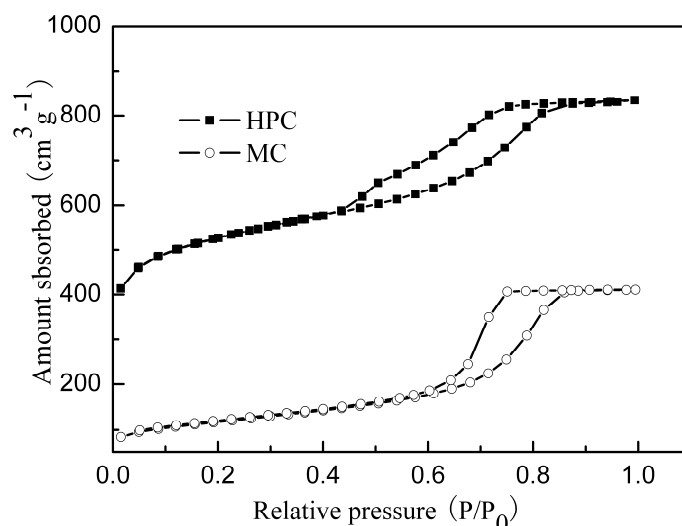


Fig. 2 N₂ adsorption-desorption isotherm of as-prepared MC and HPC sample

Table 1 Pore structural parameters of as-prepared MC and HPC sample

Sample	S_{BET}^a (m ² g ⁻¹)	S_{meso}^b (m ² g ⁻¹)	S_{micro}^c (m ² g ⁻¹)	V_T^d (cm ³ g ⁻¹)
MC	400	333	108	0.48
HPC	1661	904	1105	1.29

^a BET (Brunauer-Emmett-Teller) surface area; ^b Mesopore surface area; ^c Micropore surface area;

^d Total pore volume;

The electrocatalytic activity of HPC electrode can be studied by using electrochemical impedance spectroscopy. Nyquist plot for HPC electrode measured in a symmetric thin layer cell (shown in Fig. 3a) is displayed in Fig. 3b. In the equivalent circuit for this type of cells described in Fig. 3c, the charge-transfer resistance (R_{ct}), which can characterize the electrocatalytic activity of HPC electrode for triiodide reduction, can be obtained from the diameters of the semicircle in the high frequency region. From Fig. 3b, the R_{ct} 0.3 Ω cm² for HPC electrode is determined. A small value of R_{ct} indicates a high electrocatalytic activity of HPC electrode for triiodide reduction.

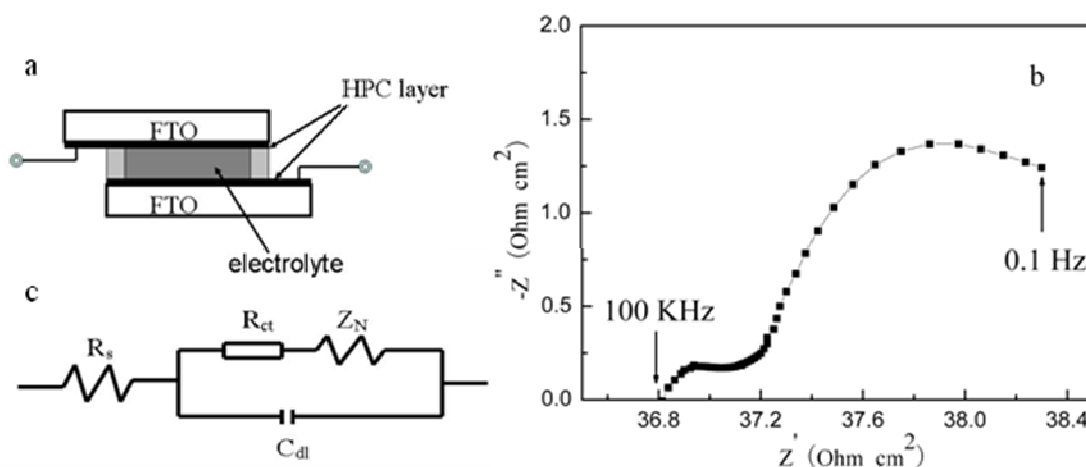


Fig. 3 (a) Electrochemical cell used for the measurement of electrochemical impedance spectroscopy. (b) Nyquist plot for HPC electrode taken at zero bias, ac amplitude 10 mV. (c) The equivalent circuit of the electrochemical cell (R_s : Ohmic serial resistance; R_{ct} : the charge-transfer resistance; C_{dl} : double layer capacitance; Z_N : Nernst diffusion resistance).

The photovoltaic performance of DSCs with HPC counter electrode was obtained under irradiation of 100 mW cm^{-2} . The photocurrent-voltage curve of DSCs with HPC counter electrode was displayed in Fig. 4. For comparison, the photocurrent-voltage curve of DSCs with conventional Pt counter electrode was also shown in Fig. 4. Pt electrode was prepared by thermal decomposition of H_2PtCl_6 on FTO glass (Pt loading is about $10 \mu\text{g cm}^{-2}$). It can be seen that DSCs based on HPC counter electrode exhibits a similar photovoltaic performance to the cell based on Pt counter electrode. The open-circuit voltage, the short-circuit current density, the fill factor and the overall conversion efficiency of DSCs based on HPC counter electrode are 0.626V, 15.44 mA cm^{-2} , 0.67 and 6.48%, respectively. The overall conversion efficiency of the device based on Pt counter electrode is 6.45%.

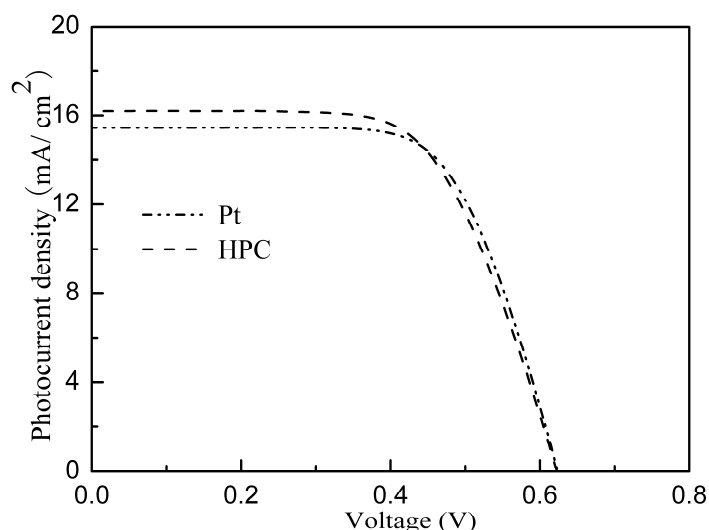


Fig. 4 The photocurrent-voltage curves of DSCs with HPC counter electrode and Pt counter electrode.

Conclusions

HPC containing abundant amounts of both micropores and mesopores were prepared by a combination of self-assembly and post activation. HPC electrode exhibited a high electrocatalytic activity for triiodide reduction. The charge-transfer resistance was $0.3 \Omega \text{ cm}^2$. The overall conversion efficiency of DSCs with HPC counter electrode was 6.48%, which is similar to that of the cell based on Pt counter electrode.

Acknowledgements

The authors appreciate the generous financial support of this work by National Science Foundation (No. 20773082).

References

- [1] B. O. Regen, M. Grätzel: Nature Vol. 353(1991), p. 737.
- [2] M. Grätzel: Nature Vol. 414(2001), p. 338.
- [3] M. Grätzel: Chem. Lett. Vol. 34(2005), p. 8.
- [4] A. Hauch, A. Georg: Electrochim. Acta Vol. 46 (2001), p. 3457.
- [5] G. Wang, R. Lin, Y. Lin, X. Xiao: Electrochim. Acta Vol. 50 (2005), p. 5546.
- [6] E. Olsen, G. Hagen, S. E. Lindquist: Sol. Energy Mater. Sol. Cells Vol. 63 (2000), p. 267.
- [7] Y. Saito, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida: J. Photochem. Photobio. A Vol. 164 (2004), p. 153.
- [8] Q. Lin, J. Wu, Q. Tang, Z. Lan, P. Li, J. Lin: Electrochem. Commun. Vol. 10 (2008), p. 1299.
- [9] T. N. Murakami, S. Ito, Q. Wang, M. K. Nazeeruddin, T. Bessho, I. Cesar, M. Grätzel: J. Electrochem. Soc. Vol. 153 (2006), p. A2255.
- [10] K. Suzuki, M. Yamaguchi, M. Kumagai, S. Yanagida: Chem. Lett. Vol. 32 (2003), p. 28.
- [11] Z. Huang, X. Liu, K. Li, D. Li, Q. Meng: Electrochem. Commun. Vol. 9 (2007), p. 596.
- [12] G. Wang, W. Xing, S. Zhuo: J. Power Sources Vol. 194 (2009), p. 568.
- [13] E. Ramasamy, J. Lee: Chem. Commun. 46 (2010), p. 2136.

Aluminum-Doped Zinc Oxide as Transparent Electrode Materials

Yulong Zhang¹, Xianpeng Zhang¹, Ruiqin Tan^{2b}, Ye Yang¹,
Junhua Zhao¹, Weiyan Wang¹, Ping Cui¹ and Weijie Song^{1a*}

¹Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, No.519
Zhuangshi Road, Zhenhai District, Ningbo, 315201, China

²College of Information Science and Engineering, Ningbo University, Ningbo, No. 818 Fenghua
Road, Jiangbei District, 315211, China

^aemail: weijiesong@nimte.ac.cn, ^bemail: tanruiqin@nbu.edu.cn

Keywords: Al-doped ZnO; sputtering target; thin film; electrical; optical

Abstract. Pristine and Al-doped zinc oxide nanopowders were synthesized via a surfactant-assisted complex sol-gel method, possessing a pure ZnO phase structure and controllable grain size which was characterized by X-ray diffraction and scanning electron microscopy. Using these nanopowders, the pristine and Al-doped ZnO magnetron sputtering targets were prepared following a mold-press, cold isostatical-press and schedule sintering temperature procedure. The relative density of these as-prepared targets was tested by Archimedes' method on densitometer. All of the results were above 95 theory density percents, and the resistivity was tested on four-probe system at a magnitude of 10^{-2} Ω cm. Related pristine ZnO thin films and Al-doped ZnO thin films were fabricated by magnetron sputtering method, respectively. The pristine and Al-doped ZnO films deposited on the quartz glass by dc sputtering owned a (002) orientation with a thickness of 350 nm at a deposition power of 100 W for two hours under an argon plasma. A good optical transparency above 80% and low resistivity of 1.60×10^{-3} Ω cm were obtained with a deposition temperature of 573 K. The optical energy bandgap could be tailored by Al doping at 4 at.% Al.

Introduction

Transparent conductive oxide (TCO) films, are currently of great commercial importance for applications in transparent electrodes for flat panel displays, solar cells and organic light emitting diodes [1–3] due to its high transmittance in the visible light area (>85%), low electrical resistivity (10^{-4} Ω cm), and good adhesion to the substrates. Nowadays, ITO films are the predominant transparent electrode in these commercial applications. However, it has a relatively poor chemical stability. Most importantly, indium is an expensive and scarce element, which inhibits its commercial application in the TCO electrodes [4].

Zinc oxide (ZnO) is taken much attention in the device application because of its low cost and low growth temperature, and stability in hydrogen plasma [5]. Group- III elements (B, Al, Ga, In) doped ZnO film has been proved to own a resistivity at the order of 10^{-4} Ω cm. In addition, group- III doped ZnO films showed an excellent transparency over the visible spectrum (400–800 nm) [6]. Among these, Al-doped ZnO (AZO) film is a potential alternative candidate to ITO film due to its low cost and abundant raw materials [7]. AZO film can be fabricated using various methods, such as sol-gel [6], pulse laser deposition (PLD) [8], magnetron sputtering (MS) [9], and chemical vapor deposition (CVD) [10]. Among these, MS technology has outstanding advantages such as simple apparatus, low deposition temperature, easy control on the doping concentration, and a large deposition area. Although MS technology has been used to prepare AZO thin films, few studies focus on tailoring the properties of AZO films by the high-quality AZO magnetron sputtering targets prepared with single-phase AZO nanopowders.

In this paper, AZO nanopowders were synthesized by using a sol-gel method firstly, and then AZO sputtering targets were prepared by a cold-isostatic press and sintering process. At last, AZO thin films with various doping concentration were fabricated by using a magnetron sputtering technology.

Experimental procedures

Powders preparation. The AZO nanopowders were synthesized by the surfactant assisted complex sol-gel method with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, citric acid (CA), and polyethylene glycol (PEG) which was reported in our previous studies [11, 12]. The mixed transparent solution containing 0.03 mol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with various contents ($\text{Al}/(\text{Al} + \text{Zn}) = 0.00, 2.00, 4.00, 6.00 \text{ at.}\%$) was dissolved in 50 mL de-ionic water. After that, the solution was dripped into the 50 mL CA (0.045 mol) and PEG 2000 (0.003 mol) solution. The total volume of this solution was 100 mL. The pH of formed solution was adjusted to 1 by adding ammonia (17 wt.%). The solution was then immersed into a 353 K water bath for 4 h stirring and 4 h aging at room temperature. The transparent solution was gelled at 358 K, and it was immediately put into a vacuum container until it turned into xerol, and then the xerol was sintered in a furnace at 773 K for 4 h in air. The AZO nanopowders were milled in an agate mortar and took further annealing at 773, 1173, and 1273 K respectively for 2 h in the air. The obtained nanopowders were pressed into coin-shaped sampler at 300 MPa for the resistivity measurement.

Sputtering preparation. The powders were pressed with uniaxial pressure (60 MPa) into 15-mm pellets with the weight of 1.5 g for each sample. And then, the samples were made by isostatic cool pressing at 250 MPa for 5 minutes to increase their initial density. Finally, all samples were subjected to a furnace sintering at 1573 K for 8 hours [13] with a heating rate of 5 K/min and then cooled by cooling in the furnace to the room temperature.

Films fabrication. The AZO thin films were fabricated by using the obtained AZO targets after polishing. All films were deposited on the quartz glass ($50 \times 30 \times 1 \text{ mm}^3$) substrates. Before deposition, the quartz substrates were ultrasonically cleaned in acetone, alcohol, and de-ionic water for 10 minutes respectively. After that, all the substrates were blow-dried with nitrogen and were dealt with ultraviolet cleaning machine for 10 minutes. The films were deposited by maintaining the d.c. power to a value of 100 W, work pressure of 0.99 Pa, sputtering time of 120 minutes, deposition temperature of 573 K. All the obtained samples were cut into $15 \times 15 \text{ mm}^2$ for analysis.

Characterization. A Bruker AXS D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation at a power of 1.6 kW was employed to take X-ray diffraction (XRD) measurements. The diffraction patterns were calibrated by using the standard corundum spectra. The instrument broadening (the FWHM curve of standard corundum) was considered in the estimation of the grain size by using the Scherrer equation. The morphology was observed by using a Hitachi S-4800 field emission scanning electron microscope (FESEM). The small area composition analysis was performed by energy dispersive X-ray spectroscopy (EDX) on a Hitachi S-4800 SEM/EDX (Japan). The optical transmission spectra were measured by an ultraviolet-visible-near infrared (UV-Visible-NIR) spectrometer (Perkin Elmer Lambda 950) with a wavelength range of 200–800 nm at room temperature. The density was determined by Archimedes method with de-ionic water immersion, and the relative density was calculated by taking the density of ZnO as 5.61 g/cm^3 . Finally, the resistivity on a size of $20 \times 5 \text{ mm}^2$ sample was tested by using a four probe resistivity testing system on the Pro4-4000 (Luscas-Signatone).

Results and discussion

Characterization of Al-doped ZnO powders. Figure 1 shows the XRD patterns of AZO nanopowders with different doping concentrations. All peaks belongs to be wurtzite ZnO without any impurity. The intensity of AZO ($\text{Al}/(\text{Al} + \text{Zn}) = 1.0, 2.0, 4.0 \text{ at.}\%$) is much weaker than that of pristine ZnO , which was due to a lattice shrinkage of ZnO by Al doping and a reduction of the crystallinity of ZnO [14–16]. The SEM pictures of the ZnO nanoparticles with different doping concentrations are showed in Fig. 2. The grain size of ZnO nanoparticles decreases from ca. 100 nm (pristine ZnO) to ca. 50 nm ($\text{Al}/(\text{Al} + \text{Zn}) = 4.0 \text{ at.}\%$) with the increase of Al doping concentration. It may because Al doping inhibits the grain growth of ZnO [17]. All the obtained nanopowders were low aggregation with a narrow distribution of particle size.

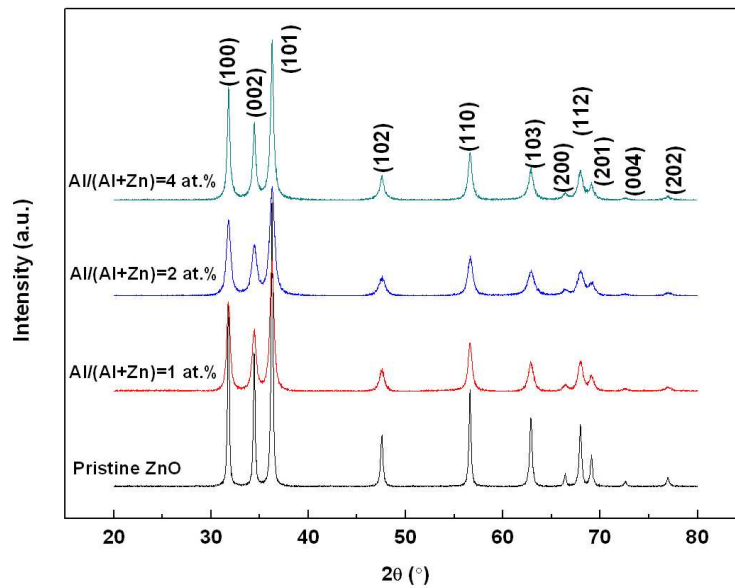


Fig. 1 XRD patterns of Al-doped ZnO nanopowders with different doping concentrations ($\text{Al}/(\text{Al}+\text{Zn}) = 0.0, 1.0, 2.0, 4.0$ at.%)

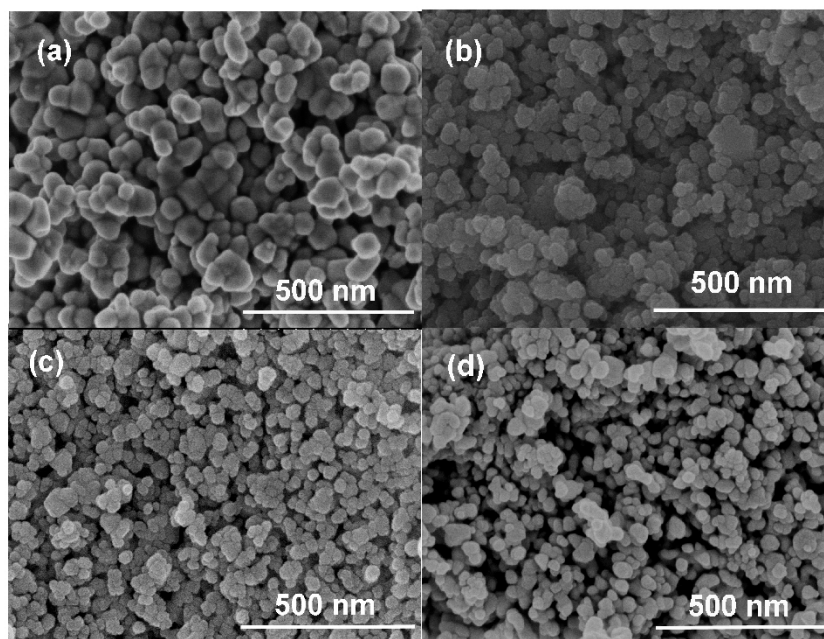


Fig. 2 SEM pictures of Al-doped ZnO nanoparticles with a doping concentration of: (a) $\text{Al}/(\text{Al}+\text{Zn}) = 0.0$ at.%, (b) $\text{Al}/(\text{Al}+\text{Zn}) = 1.0$ at.%, (c) $\text{Al}/(\text{Al}+\text{Zn}) = 2.0$ at.%, (d) $\text{Al}/(\text{Al}+\text{Zn}) = 4.0$ at.%

Characterization of Al-doped ZnO sputtering targets. AZO sputtering targets were prepared from the nanopowders obtained above. All the sputtering targets were prepared with a cold isostatic press of 300 MPa and a sintering temperature of 1573 K for 8 hours. And the XRD results of the ZnO sputtering targets with different Al doping concentrations are shown in Fig. 3. The major phase structure was the structure of wurtzite ZnO. In the spectra, the (220), (311), (511), and (440) peaks ascribed to ZnAl_2O_4 appear when the Al doping concentrations reached 1.0 at.% and above. This could be relative to the solubility of Al in ZnO. Many papers pointed that the solubility of Al in ZnO was less than 2.0 at.% [18-21]. In this study, the results show that the solubility of Al in ZnO was 0.9 at.% from the characterization from XRD and EDX which will be published in the other paper. The microstructures of the AZO sputtering targets are shown in Fig. 4. The amount of pores of the AZO sputtering targets decreases with the increase of Al doping concentrations. It could be explained by the formation of ZnAl_2O_4 particles, decreasing the sintering stress of ZnO ceramics [22].

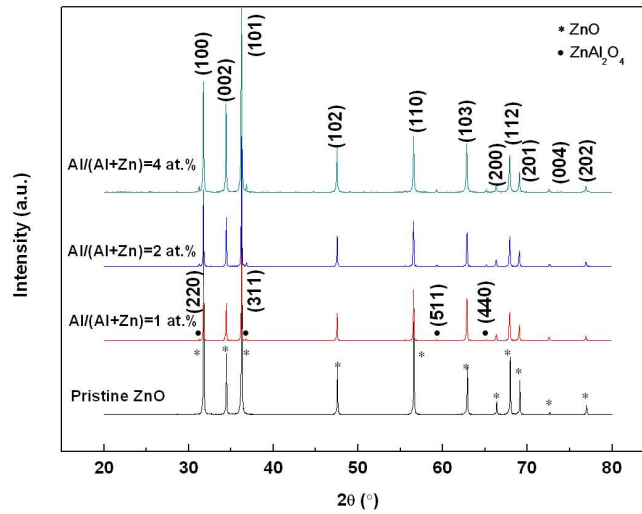


Fig. 3 XRD patterns of Al-doped ZnO sputtering targets with different Al doping concentrations ($\text{Al}/(\text{Al}+\text{Zn}) = 0.0, 1.0, 2.0, 4.0$ at.%)

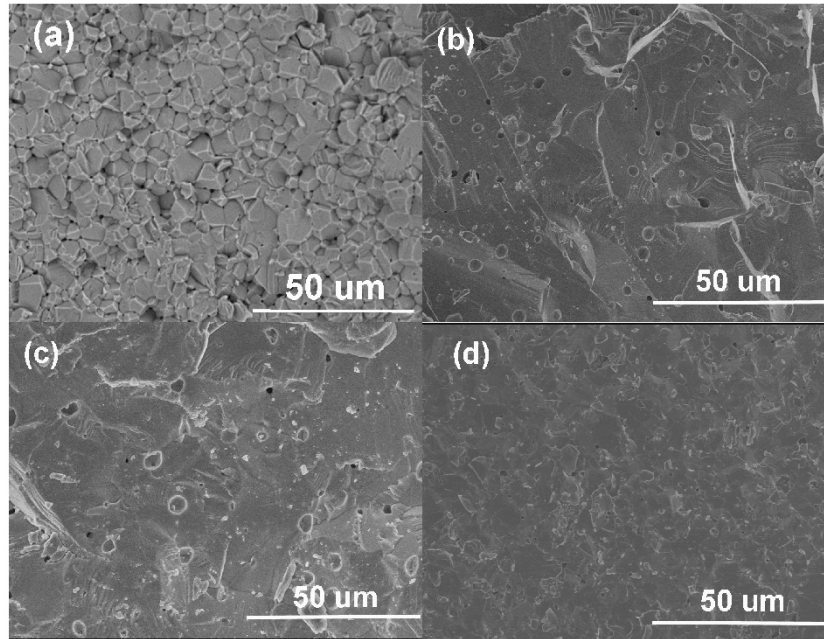


Fig. 4 SEM pictures of Al-doped ZnO sputtering targets with a doping concentration of:
 (a) $\text{Al}/(\text{Al}+\text{Zn}) = 0.0$ at.%, (b) $\text{Al}/(\text{Al}+\text{Zn}) = 1.0$ at.%,
 (c) $\text{Al}/(\text{Al}+\text{Zn}) = 2.0$ at.%, (d) $\text{Al}/(\text{Al}+\text{Zn}) = 4.0$ at.%

The density and resistivity of the AZO sputtering targets are summarized in Table 1. The density of AZO sputtering targets increases with the Al doping concentration, and reach a maximum of 98.9% at a doping concentration of $\text{Al}/(\text{Al}+\text{Zn}) = 4.0$ at.%. The densification mechanism of AZO ceramics was reported in the previous studies. It could be considered as two reasons as follows. On one hand, Al doping could retard the densification of ZnO by reducing the sintering stress. On the other hand, Al doping could significantly inhibit the grain growth of ZnO. Since the densification rate was inverse proportional to the particle size, this grain growth inhibition effect increases the densification rate. These two competing effects on the densification coexist in the sintering of AZO which could explain the contribution of Al doping in the densification of AZO samples [13]. The resistivity of sputtering targets reduced from 7.6×10^7 (pristine ZnO) to $1.2 \times 10^{-2} \Omega \text{ cm}$ (1.0 at.%), while it increased to $3.6 \times 10^{-2} \Omega \text{ cm}$ when the Al doping concentration was up to 4.0 at.%. The resistivity of obtained AZO

targets ($10^{-2} \Omega \text{ cm}$) is much lower than that of pristine ZnO ($10^7 \Omega \text{ cm}$), which was due to the substitution of Zn by Al, and producing excessive carrier in the sintered ceramics. However, when the Al doping concentration exceeded 1.0 at.%, the ZnAl_2O_4 particles could be formed at the grain boundaries of ZnO and inhibit the transport of free carriers, and increase the resistivity.

Table 1 Density and resistivity of the Al-doped ZnO sputtering targets

Al/(Al+Zn) atomic ratio percents	0.0 at.%	1.0 at.%	2.0 at.%	4.0 at.%
Relative density (ZnO: 5.61 g/cm^3)	95.2	96.7	97.1	98.9
Resistivity ($\Omega \text{ cm}$)	7.6×10^7	1.2×10^{-2}	1.5×10^{-2}	3.6×10^{-2}

Characterization of Al-doped ZnO thin films. The AZO thin films were subsequently deposited on quartz substrates by using the obtained targets. The XRD results of the deposited thin films are shown in Fig. 5. All films well possess (002) orientation with a low-intensity (004) orientation. The films were dense with a thickness of about 350 nm. Here, the picture of the AZO film with a doping concentration of 4.0 at.% is shown in Fig. 6. The surface of the film shown in Fig. 6(a) is densely bristled with irregular shape particles. And the section profile was dense and smooth as shown in Fig. 6(b).

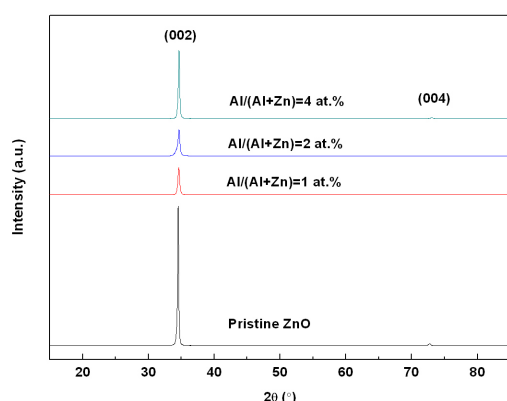


Fig. 5 XRD patterns of Al-doped ZnO films with the various Al doping concentration

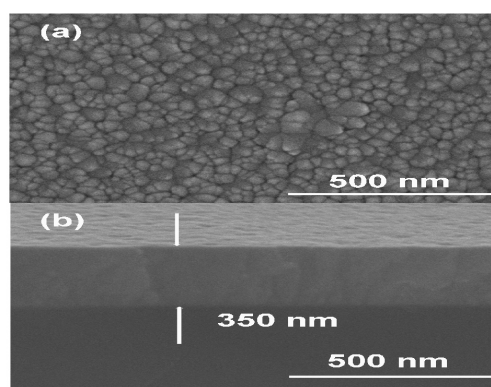


Fig. 6 SEM pictures of Al-doped ZnO films (a) surface profile, (b) section profile

The resistivity of the obtained films is summarized in Table 2. The resistivity of AZO thin films decrease from 9.5×10^4 to $1.60 \times 10^{-3} \Omega \text{ cm}$ with the increase of Al doping concentration, which could be explained by the Al taking the substitute position of Zn, and offering excessive free carrier which could contribute to the resistivity decrease.

Table 2 Resistivity of ZnO thin films with different Al doping concentration

Al/(Al+Zn) atomic ratio percents	0.0 at.%	1.0 at.%	2.0 at.%	4.0 at.%
Resistivity ($\Omega \text{ cm}$)	9.5×10^4	9.2×10^{-3}	3.4×10^{-3}	1.60×10^{-3}

The transmittance spectra (wavelength range of 200–1700 nm) of the obtained films are shown in Fig. 7. The average transmittance of each film is over 80% at a wavelength range of 400–800 nm. The inset in Fig. 7 is the transmittance spectrum with a wave length from 300 nm to 500 nm. The absorption edge has a consistent blue shift from 370 (pristine ZnO) to 333 nm ($\text{Al}/(\text{Al}+\text{Zn})=4.0 \text{ at.}\%$), which indicates an increase of optical energy band from 3.36 eV (pristine ZnO) to 3.73 eV ($\text{Al}/(\text{Al}+\text{Zn})=4.0 \text{ at.}\%$) as shown in Fig. 8. This could be because of the Moss-Burstein effect caused by Al doping [23].

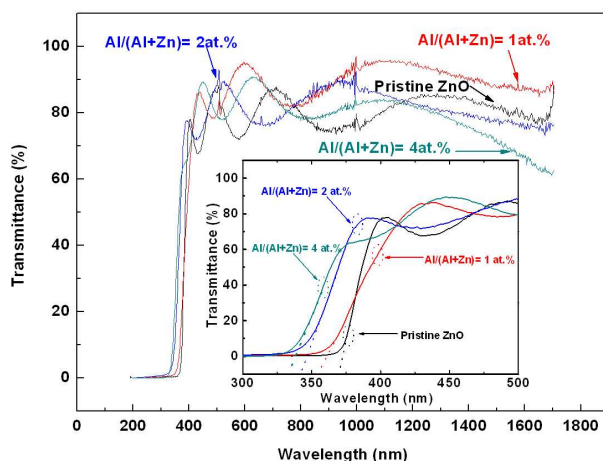


Fig. 7 Transmittance spectra of Al-doped ZnO thin films with different Al doping concentration. The inserted was the transmittance spectra at a wavelength range of 300–500 nm

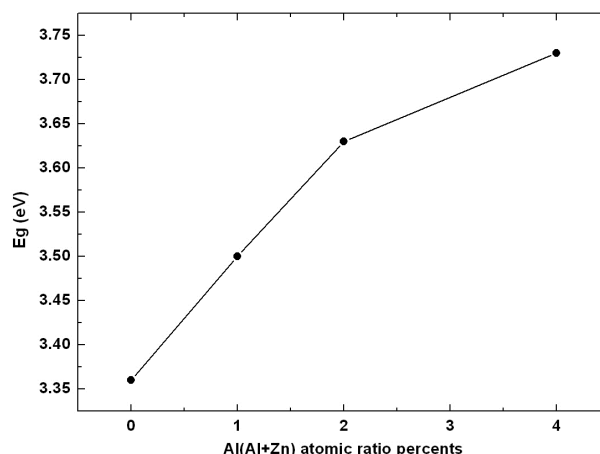


Fig. 8 Optical energy bands of Al-doped ZnO films were calculated from the transmittance spectra of AZO thin films with different Al doping concentrations.

Conclusions

In this paper, AZO transparent conductive films were deposited by magnetron sputtering method with the AZO sputtering targets prepared by the AZO nanopowders synthesized by the sol-gel technology. Wurtzite AZO nanoparticles were obtained without any impurity. The AZO nanopowders were low aggregation with a mean particle size of ca. 50 nm while 100 nm for the pristine ZnO. High density and low resistivity AZO sputtering targets were obtained with an existence of ZnAl_2O_4 phase. Dense and well (002) orientation AZO thin films were deposited with a thickness of 350 nm. The resistivity of the films decreased with the increase of Al doping concentration, and reached a minimum of $1.60 \times 10^{-3} \Omega \text{ cm}$ at the Al doping content of 4 at.%. The average transmittance of all the films was above 80% at the wavelength range of 400–800 nm. The transmittance spectra showed a consistent blue shift from 370 to 333 nm due to Al doping, and resulted in an optical energy increase from 3.36 to 3.73 eV.

Acknowledgements

Financial supports from the Hundred Talents Program, the Solar Action Program, and the Innovative Research International Partnership Program of Chinese Academy of Sciences, the Ningbo Innovative Research Team Program, the Ningbo Natural Science Foundation (No. 2009A610058) and the Zhejiang Natural Science Foundation (Y407364) are highly appreciated.

References

- [1] C.H. Cheung, W.J. Song and S.K. So: Organic Electronics Vol. 11 (2010), p. 89
- [2] A. Solieman, A.H. Moharram and M.A. Aegeeter: Appl. Surf. Sci. Vol. 256 (2010), p. 1925
- [3] D.Y. Wan, F.Q. Huang, Y.M. Wang, X.L. Mou and F.F. Xu: Appl. Mater. Inter. Vol. 2 (2010), p. 2147
- [4] H. Zhu, J. Hüpkes, E. Bunte, A. Gerber and S.M. Huang: Thin Solid Films Vol. 518 (2010), p. 4997
- [5] H. Zhou, G.J. Fang, L.Y. Yuan, C. Wang, X.X. Yang, H.H. Huang, C.H. Zhou and X.Z. Zhao: Appl. Phys. Lett. Vol. 94 (2009), p. 013503
- [6] M.W. Zhu, J. Gong, C. Sun, J.H. Xia, and X. Jiang: J. Appl. Phys. Vol. 104 (2008), p. 073113
- [7] T. Tohsophon, J. Hüpkes, H. Siekmann, B. Rech, M. Schultheis, N. Sirikulrat: Thin Solid Films Vol. 516 (2008), p. 4628
- [8] L. Gong, Z.Z. Ye, J.G. Lu, L.P. Zhu, J.Y. Huang, X.Q. Gu, and B.H. Zhao: Vacuum Vol. 84 (2010), p. 947
- [9] J.M. Kim, P. Thiagarajan, and S.W. Rhee: Thin Solid Films Vol. 518 (2010), p.5860
- [10] F. Ruske, M. Roczen, K. Lee, M. Wimmer, S. Gall, J. Hüpkes, D. Hrunski, and B. Rech: J. Appl. Phys. Vol. 107 (2010), p. 013708
- [11] Y.L. Zhang, Y. Yang, J.H. Zhao, R.Q. Tan, P. Cui, and W.J. Song: J. Sol-gel. Sci. Technol. Vol. 51 (2009) p. 198
- [12] Y.L. Zhang, Y. Yang, J.H. Zhao, R.Q. Tan, W.Y. Wang, P. Cui, and W.J. Song: J. Mater. Sci., (2010), DOI 10.1007/s10853-010-4813-9
- [13] J.P. Han, P.Q. Mantas, and A.M.R. Senos: J. Mater. Res. Vol. 16 (2001), p. 459
- [14] P. Kadam, C. Agashe, and S. Mahamuni: J. Appl. Phys. Vol. 104 (2008), p. 103501
- [15] K.C. Park, D.Y. Ma, and K.H. Kim: Thin Solid Films Vol. 305 (1997), p. 201
- [16] S.C. Navale, V. Ravi, I.S. Mulla, S.W. Gosavi, and S.K. Kulkarni: Sens. Actuators, B Vol. 126 (2007), p. 382
- [17] M. Mazaheri, A.M. Zahedi, and S.K. Sadrnezhad: J. Am. Ceram. Soc. Vol. 91 (2008), p. 56
- [18] K. Zhirouzu, T. Kawamoto, N. Enomoto, and J. Hojo: Jpn. J. Appl. Phys. Vol. 49 (2010), p.010201
- [19] K. Zhirouzu, T. Ohkusa, M. Hotta, N. Enomoto, and J. Hojo: J. Ceram. Soc. Jpn. Vol. 115 (2007), p. 254
- [20] H. Serier, M. Gaudon, and M. Ménétrier: Solid State Sci. Vol. 11 (2009), p. 1192
- [21] J.P. Wiff, Y. Kinemuchi, and K. Watari: Mater. Lett. Vol. 63 (2009), p. 2470
- [22] P.L. Chen and I.W. Chen: J. Am. Ceram. Soc. Vol. 89 (1997), p. 637
- [23] C. Jeong, H.S. Kim, D.R. Chang, and K. Kamisako: Jpn. J. Appl. Phys. Vol. 47 (2008), p. 5656

Study on determination of I-V curve of dye-sensitized solar cell

Hanmin Tian^{1,2, a}, Tao Yu^{1, b*} and Zhigang Zou¹

¹ Eco-materials and Renewable Energy Research Center (ERERC), Department of Physics, Nanjing University, Nanjing 210093, China;

² Department of Electronic Science and Technology, School of Information, Hebei University of Technology, Tianjin 300401, China;

^atianhanmin@hebut.edu.cn, ^byutao@nju.edu.cn*

Key words: Dye-sensitized solar cell; Equivalent circuit; EIS; Internal resistance

Abstract. Many studies reported that dye-sensitized solar cells have more significant capacitance characteristics than the silicon solar cell. In this study, it was found the capacitance characteristics of dye-sensitized solar cell changes with the imposed bias voltage. The bias voltage is indispensable in the standard measurement for the conversion efficiency of dye-sensitized solar cell. The influence of changed capacitance during the measurement on the conversion efficiency of dye-sensitized solar cells was investigated. The analysis on the EIS spectra and equivalent circuit shows that the capacitance of dye-sensitized solar cells is small and the deviation cell I-V characteristics from the steady-state value is minor when the applied bias is small; while under a condition with a large applied bias, the capacitance characteristics of dye-sensitized solar cell grew rapidly and the I-V characteristics deviated from the steady-state value significantly increased. This phenomenon is helpful for the accurate measurement of the quantum conversion efficiency and photoelectric conversion efficiency of dye-sensitized solar cells.

Introduction

Dye-sensitized solar cells (DSSCs) have been extensively studied in the last decade as one of the most promising solar cells due to their low cost and simple process of manufacture [1,2]. In order to accurately evaluate the materials, structures and manufacture of DSSC, an exact measurement method on DSSCs' photovoltaic character is necessary. It was reported the traditional monochromatic incident photon-to-electron conversion efficiency (IPCE) measurement method in previous studies, such as the American Society for Testing and Materials standard (ASTM), is not suitable for measuring the IPCE of dye-sensitized solar cells (DSSCs) [3]. The quantitative analysis, which is based on equivalent circuits and parameter estimation, proved the existence of capacitance characteristics in DSSCs causing the fluctuation of the measured IPCE. On the other hand, I-V performance is the most direct way to obtain the entire photoelectric conversion efficiency of solar cells [4-6], but the results need further explanation. According to the experimental results and quantitative analysis in this study, I-V performances of DSSC were influenced by the capacitance characteristics of the DSSC.

Analysis of the previous results

Dye-sensitized solar cells were prepared as the typical method as reported [11]. The DSSC I-V curve is displayed in Fig. 1. It was found that the DSSC I-V curve changes dramatically upon variation of the speed of bias power supply stepwise change, while no significant change could be observed in that of silicon cells (Fig. 2). The stepwise change of bias power supply is described by T_d , T_m , and ΔV , which are sampling delay time, measuring integration time, and step source level, respectively. This interesting phenomenon shows that dye-sensitized solar cells have a different nature with silicon solars. According to our previous experience [3], is the result of capacitive properties, but it should be proved.

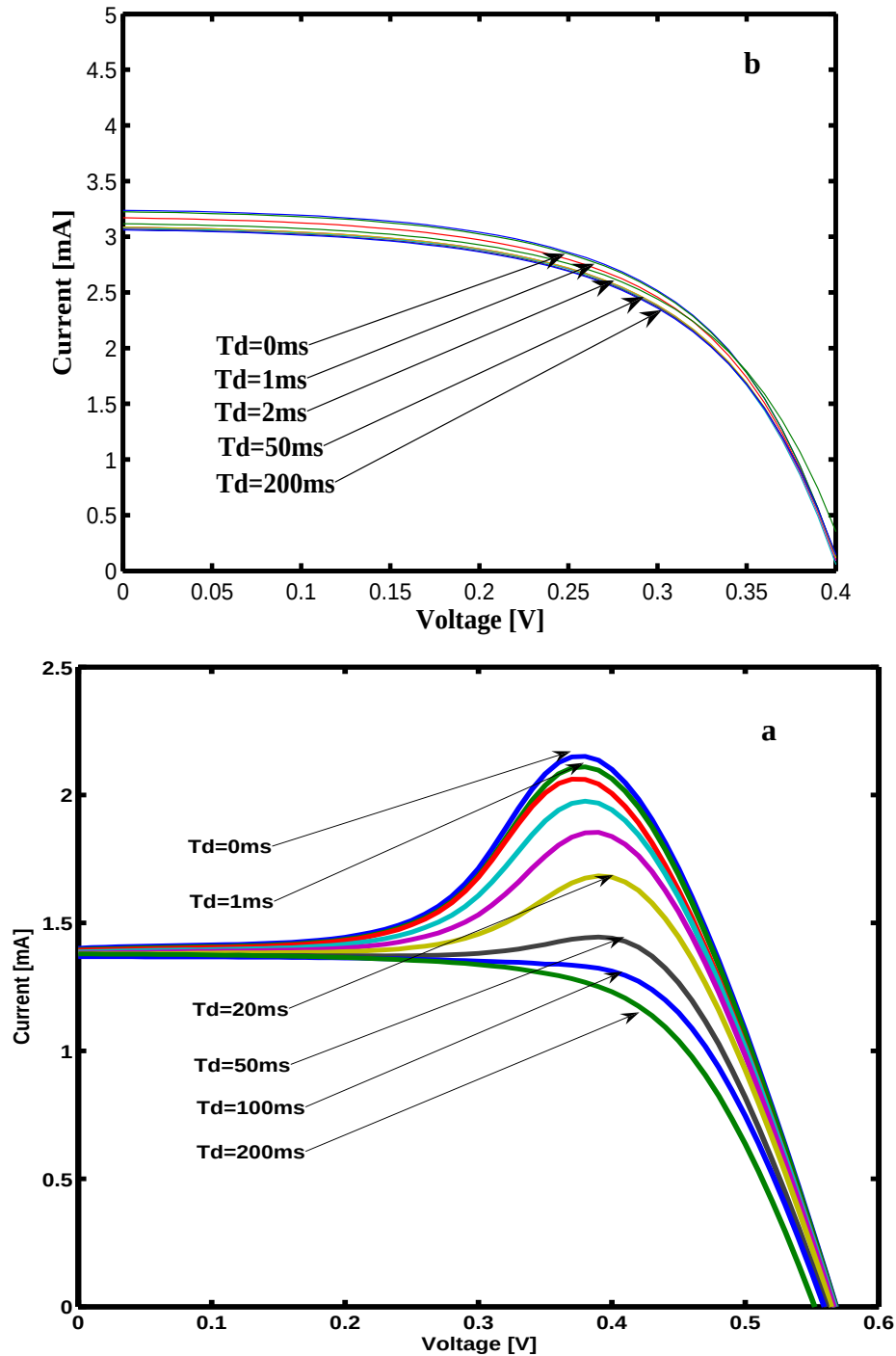


Fig.1. a) Measured I-V curves of DSSC in different stepwise change speeds
b) Measured I-V curves of Si cell in different stepwise change speeds

Scholars have reported the capacitance in DSSC much more significant than Si cell [7-12], which are thought sourcing from the existence of double-charged layer (Helmholtz layer) at the interface of porous semiconductor electrode and electrolyte of DSSC [7,12,13]. Though Si cell processes capacitance characteristic which sources from its junction capacitor, this capacitance is proposed being ignored for its minuteness [14,15].

The capacitance characteristic are also unique components of DSSCs' equivalent circuit in comparison with the that of Si cells [16,17], as shown in Fig. 2, for equivalent circuit models have been largely investigated for analyzing the electrical processes involved in the solar cell [18-21]. According to the mathematical calculation of equivalent circuit, we can get the influence of capacitance of DSSCs on its I-V curve from a mathematical point of view.

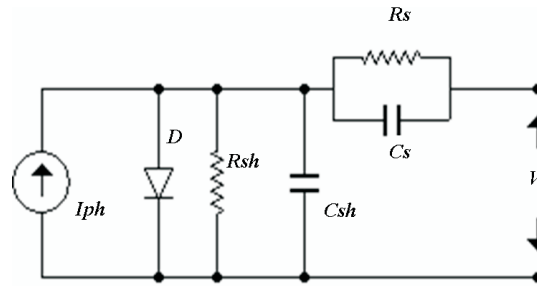


Fig.2. The equivalent circuits of DSSC

Based on the equivalent circuit, equations 1 are deduced according to Kirchhoff's law [22] as follows:

$$I = I_{ph} - I_0 \cdot \left(\exp\left(\frac{q}{K \cdot T \cdot n} \cdot (V(t) + I \cdot R_s)\right) - 1 \right) - \frac{(V(t) + I \cdot R_s)}{R_{sh}} + (C_s + C_{sh}) \cdot R_s \cdot \frac{d(I)}{d(t)} + C_{sh} \cdot \frac{dV(t)}{d(t)} \quad (1)$$

The current expression with capacitance performance has been derived as equation 1. I_0 initial current; R_s series resistance; R_{sh} parallel (shunt) resistance; T temperature; n diode factor; q elementary electric charge; K Boltzmann constant; C_s series capacitance; C_{sh} parallel (shunt) capacitance; I_{ph} photo current.

The derivative of voltage to time, $dV(t)/d(t)$, is multiplied with capacitance C_{sh} , as an algebraic term of equation 1. Therefore, scanning speed $dV(t)/d(t)$ is one of the most important factors in determining the output value I of DSSCs. What can be concluded directly from equation 1 is that, the output value I would be distorted when the scanning speed varies. The more capacitance characteristic in DSSCs, the greater the influence of scanning speed plays on the measured I - V curve. If the capacitance of the cell is 0, there will be no value containing $d(t)$ in equation 1 and the scanning speed will not affect the I - V curve of the cell anymore.

According to the measured I - V data, as shown in Fig. 1, the parameters of equivalent circuit in equation 1 are obtained by mathematical estimation, which is shown below:

C_s	0.0728 mF	R_s	38.6Ω	n	1.59	I_{ph}	1.39 mA
I_0	0.21e-5 mA	C_{sh}	0.261 mF	R_{sh}	8351.9Ω		

The estimation method is described as follows. First, we assign a set of initial values to the equivalent circuit parameters equation 8, and then assess the difference between $I(t)$ and measured data. If the difference is significant, the next group of new parameter values will be optimized by Newton-Raphson's method, and further evaluation will be performed until the most suitable parameters are obtained.

According to the estimated circuit parameter value, the influence of scanning speed and the capacitance characteristic of DSSCs on the I - V curve are calculated. The calculated results (Fig. 3) are consistent with the experimental results (Fig. 1). The calculated I - V curves exhibit uplift around the maximum power point when the scanning speed increases. When T_d is longer than 200 ms, the I - V curves almost lap over each other without any perceptible uplift. Under the same condition, the I - V curve of DSSCs which have greater value of capacitance shows more observable uplift phenomena. For the DSSCs with different morphologies and parameter values, the appropriate speeds of bias power supply's stepwise change in I - V measurement should be different. But we found that results are not fully reproductive to the experimental results: at the initial scan when external bias is small (about 0V to 0.25V), experimental bias is far less than the calculated bias. Therefore, we should further analysis the reasons for such discrepancies.

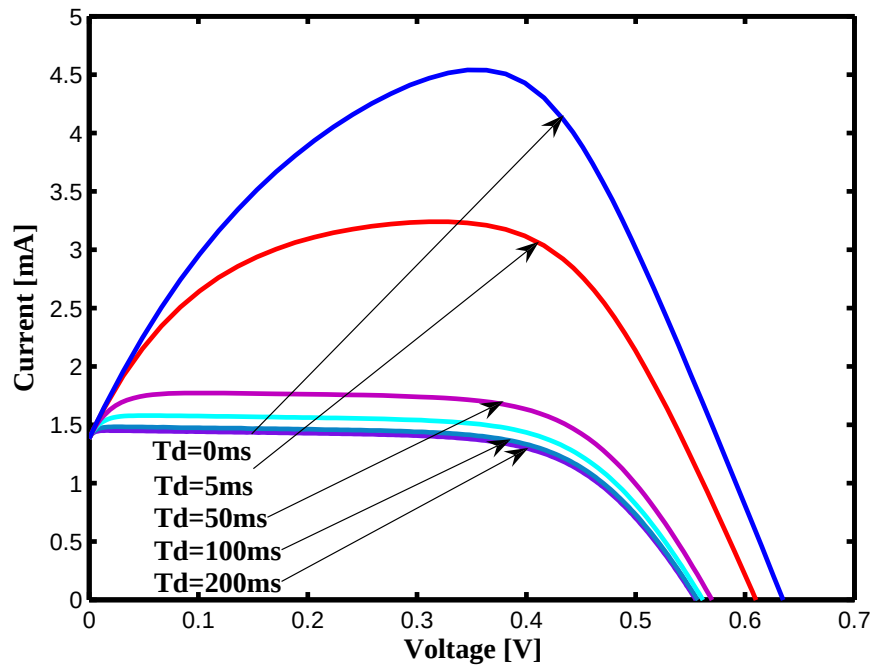


Fig.3. The time-dependence characteristic of DSSC I-V curves by the theoretical analysis

Development of a precise method to determine I-V curve of DSSCs and its application

In further experiments, it was found the capacitance characteristics of DSSCs were changed with bias voltage. The EIS spectra of DSSC with bias voltage and that without bias voltage were shown in Fig. 4, by PARSTAT 2273, Princeton Company. The perturbation amplitude was 5mV and scanning range was 10M-100 KHz. The results showed the capacitance of DSSC is much larger than that of Si. And furthermore, a more noteworthy phenomenon was that, when putting bias voltage of 0.5V on DSSC, its capacitance impedance became more prominent (Fig. 4 the curve pluses *).

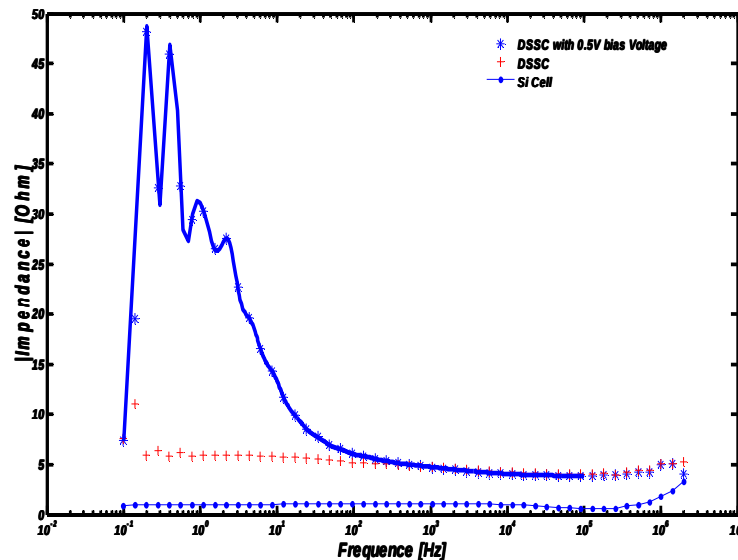


Fig.4. DSSC and Si solar cell' EIS spectrum

This EIS results mean the capacitance characteristics of DSSC in the I-V measurement should be further highlighted, because the I-V measurement method need applying gradually changed *bias voltage* on the measured cell necessarily. During the measurement process, capacitance would not be constant. Therefore, we are more inclined to renew the traditional equivalent circuit of DSSC,

with value-changed capacitors instead of value-fixed capacitors, and also change equations 1 with the value-changed capacitors. We introduce a variable factor $(1 + a_m \cdot V(t))^{b_m}$ to the equation 1, in which $m = s$ or sh . In this way, equation 2 is got.

$$I = I_{ph} - I_0 \cdot \left(\exp\left(\frac{q}{K \cdot T \cdot n} \cdot (V(t) + I \cdot R_s)\right) - 1 \right) - \frac{(V(t) + I \cdot R_s)}{R_{sh}} + \left[(1 + a_s \cdot V(t))^{b_s} \cdot C_s + (1 + a_{sh} \cdot V(t))^{b_{sh}} \cdot C_{sh} \right] \cdot R_s \cdot \frac{d(I)}{d(t)} + (1 + a_{sh} \cdot V(t))^{b_{sh}} \cdot C_{sh} \cdot \frac{dV(t)}{d(t)} \quad (2)$$

Where coefficient a_m and b_m characterize the change of DSSC's capacitor with the bias voltage. When a_m and b_m equal to 0, the value of capacitance is fixed; when b_m is 0, the capacitance changes linearly with the bias voltage; when a_m and b_m do not equal to 0, the capacitance changes with voltage exponentially.

According to the previous estimated value of equivalent circuit parameters, the I-V performance was calculated by equation 2 renewedly, which introduces variable capacitors. Here, a_m and b_m were employed to 0.5 and 18, so that during the applied bias voltage scanned from 0 to 0.5 voltage, the variable factor $(1 + a_m \cdot V(t))^{b_m}$ is about 25. Such increase of capacitance in calculation is consistent with the magnitude of capacitance change in EIS experiments. Calculation results were shown in Fig. 5.

What could be found in Fig. 5 is that, the estimation of I-V performance and the experimental I-V performance (shown in Fig 1) were more consistent after considering the capacitance changes of DSSC during the I-V measurement. In turn, the experimental I-V performance, with the confirmation of mathematical calculation, also verified the EIS finding that the cell capacitances were changed with bias voltage.

The marked and changed capacitance of DSSCs in I-V testing should be considered in testing standards for this type cell. For example, it involves the I-V measurement speed, step source level and other performances about capacitive resonance.

There are still some disaccord between the calculation and experiment, especially the estimated open circuit voltages were larger than the experimental results when sampling delay time T_d less than 5ms. Such problem needs further in-depth analysis, for these related foundations are not mature, such as the motion rule in nano-level porous channels, the electrolyte adsorption and reaction of such micro-areas, especially the related nano- or micro-fluid physics, mechanics, surface physics and chemistry are still unclear, far from the level as macro-level linearity equivalent circuit. The capacitance-related phenomenon observed in this paper should be an interesting content in future research.

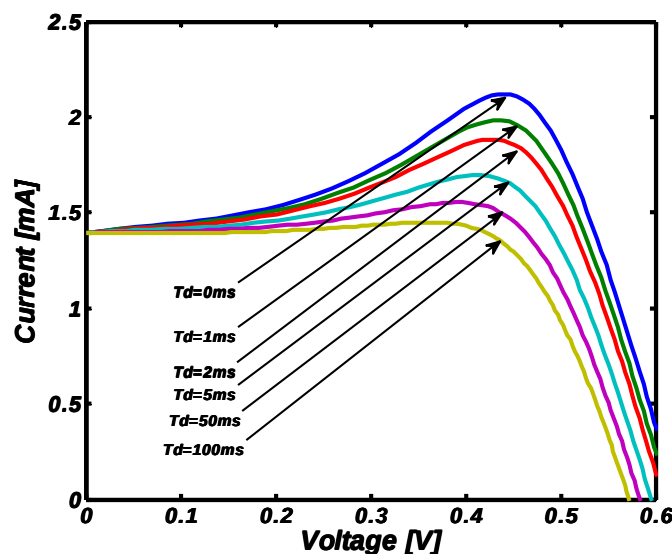


Fig.5. The calculated I-V curves of DSSC including its changed capacitance characteristics

Conclusions

The marked and changed capacitance characteristics of dye-sensitized solar cell following with the bias voltage which imposed on it were analyzed. The influence of changed capacitance of dye-sensitized solar cells to the measurement of dye-sensitized solar cell I-V performance was proved. When the applied bias voltage is small and in a certain scan rate, the dye-sensitized solar cells capacitance characteristics is small, and the cell I-V characteristics deviation from the steady-state value is minor; while following larger applied bias voltage, the capacitance characteristics of dye-sensitized solar cell growth rapidly, and the I-V characteristics deviate from the steady-state value significantly increased. This phenomenon is helpful for the accurate measurement of the photoelectric conversion efficiency of dye-sensitized solar cells.

Acknowledgements

The authors would like to acknowledge financial support from the National Natural Science Foundation of China (Nos 20603017 and 20528302), as well as the Jiangsu Provincial High Technology Research Program (No. BG2006030). We would like to thank Mr. Zhang Haitao and Mr. Zhang Jiyuan for their helpful discussions. Professor Zou and Yu would like to thank the Jiangsu Provincial Talent Scholars Program.

References

- [1] Gratzel, M., Cluster Physics - All Surface and No Bulk. *Nature* Vol.349 (1991), p. 740
- [2] Nazeeruddin, M.K., et al., Combined Experimental and DFT-TDDFT Computational Study of Photoelectrochemical Cell Ruthenium Sensitizers. *Journal of the American Chemical Society* Vol.127 (2005), p. 16835
- [3] Hanmin, T. and et al., Influence of capacitance characteristic on dye-sensitized solar cell's IPCE measurement. *Journal of Physics D: Applied Physics* Vol. 42 (2009),p. 045109
- [4] Zhang, J.J., et al., Study on Zn(II) tetracarboxy phthalocyanine doped TiO₂ electrode using electrochemical impedance spectrum. *Acta Physico-Chimica Sinica* Vol.24 (2008),p. 79
- [5] [Murayama, M. and T. Mori, Equivalent circuit analysis of dye-sensitized solar cell by using one-diode model: Effect of carboxylic acid treatment of TiO₂ electrode. 3rd International Conference on Molecular Electronics and Bioelectronics Vol.1 (2005),p. 542
- [6] Fang, X., et al., Effect of the thickness of the Pt film coated on a counter electrode on the performance of a dye-sensitized solar cell. *Journal of Electroanalytical Chemistry* Vol.570 (2004),p. 257
- [7] Schwarzburg, K. and F. Willig, Origin of photovoltage and photocurrent in the nanoporous dye-sensitized electrochemical solar cell. *Journal of Physical Chemistry B* Vol.103 (1999),p. 5743
- [8] Queisser, H.J., Photovoltaic conversion at reduced dimensions. *Physica E: Low-dimensional Systems and Nanostructures* Vol.14 (2002),p. 1
- [9] Kuang, D.B., et al., High-efficiency and stable mesoscopic dye-sensitized solar cells based on a high molar extinction coefficient ruthenium sensitizer and nonvolatile electrolyte. *Advanced Materials* Vol. 19 (2007),p. 1133
- [10] Nozik, A.J. and R. Memming, Physical Chemistry of Semiconductor/Liquid Interfaces. *The Journal of Physical Chemistry* Vol. 100 (1996),p. 13061
- [11] Hanmin, T., et al., An improved method to estimate the equivalent circuit parameters in DSSCs. *Solar Energy* Vol.83 (2009),p. 715

-
- [12] Schwarzburg, K. and F. Willig, Diffusion Impedance and Space Charge Capacitance in the Nanoporous Dye-Sensitized Electrochemical Solar Cell. *The Journal of Physical Chemistry B* Vol.107 (2003),p. 3552
- [13] Allen J. Bard, M.S., Stuart Licht,, *Encyclopedia of Electrochemistry, Chapter 1 Fundamentals of Semiconductor Electrochemistry and Photoelectrochemistry*, Wiley-VCH, Weinheim, (2001),p. 28
- [14] Chan, H.C., et al., Exact Eguivalent Circuit Model for Steady - State Characterization of Semiconductor Devices with Mutiple- Energy- Level Recombination Centers. *IEEE ED Vol.* 26 (1979),p. 924
- [15] Martin A Green, *Solar Cells-Operating Principle, Technology and System Application*. N. J.: Prentice Hall, Inc. Englewood Cliffs Vol.4 (1998),p. 249
- [16] Nogueira, A.F., C. Longo, and M.A. De Paoli, Polymers in dye sensitized solar cells: overview and perspectives. *Coordination Chemistry Reviews* Vol.248 (2004),p. 1455
- [17] Mora-Sero, I., et al., Implications of the negative capacitance observed at forward bias in nanocomposite and polycrystalline solar cells. *Nano Letters* Vol.6 (2006),p. 640
- [18] Ruhle, S. and D. Cahen, Electron tunneling at the TiO₂/substrate interface can determine dye-sensitized solar cell performance. *Journal of Physical Chemistry B* Vol.108 (2004),p. 17946
- [19] Asano, T., T. Kubo, and Y. Nishikitani. Electrochemical properties of dye-sensitized solar cells fabricated with PVDF-type polymeric solid electrolytes. in *International Conference on Photochemistry*. 2003. Nara, JAPAN: Elsevier Science Sa.
- [20] Zhang J, et al., Conductive carbon nanoparticles hybrid PEO/P(VDF-HFP)/SiO₂ nanocomposite polymer electrolyte type dye sensitized solar cells. *Solid State Ionics* Vol.178 (2007),p. 1595
- [21] Koide, N., et al., Improvement of efficiency of dye-sensitized solar cells based on analysis of equivalent circuit. *Journal of Photochemistry and Photobiology a-Chemistry* Vol.182 (2006),p. 296
- [22] Johnson, D.H., Origins of the equivalent circuit concept: the current-source equivalent. *Proceedings of the IEEE* Vol.91 (2003),p. 817

Effect of the residual template on surface photoelectric characteristics of structurally-ordered macroporous nanocrystalline TiO₂

Sailing Wei, Kuiying Li, Weiyong Yang, Chunmei Wang, Jian Zhang

State Key Lab of Metastable Materials Science and Technology, Yanshan University,
Qinhuangdao Hebei Province 066004, China;

Email: kuiyingli@ysu.edu.cn

Keywords: macroporous; nanocrystalline TiO₂ thin film; PS template; SPV; PA; residual template.

Abstract. The macroporous nanocrystalline TiO₂ thin film was prepared by dipping-coating method. Polystyrene (PS) microspheres template was used as pore-forming assistant and TiO₂ sol was used as precursor. The photoelectric characteristics of the samples were studied using surface photovoltage (SPV) and photoacoustic (PA) techniques. The presence of a small amount of residual template damages the integrity of the porous TiO₂ film with inverse opal structure, and TiO₂ may be restricted in certain application fields as photonic crystals. A small amount of residual template changes the surface photovoltaic properties of the porous TiO₂ film, resulting mainly in the broadened scope and the increased intensity of SPV response.

Introduction

Following Yablonovich [1] and John [2] the research into photonic crystals has generated considerable attention because of potential applications in the fields of photonic and photoelectronic devices, and optical communications. As it is well known, photonic crystal is a kind of materials that has periodic dielectric structures exhibiting a complete photonic band gap (PBG) [3-7]. Nanocrystalline TiO₂ thin film with order macroporous structure has narrow pore diameter distribution and good periodicity properties except for a high ratio of refractive indexes of TiO₂ and air [8-10]. In numerous preparations of PBG materials, template method is more convenient and effective way [11, 12]. In the recent two decades, ones paid more attentions to control pore structures, add defect states, and improve light transmitting characteristic in terms of the PBG material obtaining by template method [13-16]. However, the effect of residual template on photoexcited charge transfer (CT) transition behaviors of the order macroporous nano-TiO₂ thin film has not been reported. In the present paper, the order macroporous nano-TiO₂ thin film was prepared by a dipping-pulling technique, in which PS was used as template, and nano-TiO₂ sol as a precursor. The photoelectric characteristic of the samples were probed by SPV and PA technologies.

Experimental

Preparation of the samples. In the present paper, we have synthesized single scattered polystyrene (PS) spheres in the method of emulsifier-free polymerization. The PS templates were assembled by dipping-coating method. A clear FTO glass substrate was settled vertically into the emulsion of PS for 5 minutes, and then drew slowly it out from the emulsion. The TiO₂ sol was prepared by sol-gel method. Then dip the PS template vertically into the TiO₂ sol for 3 minutes, and drew slowly it out from the sol. Dry it out under the room temperature. Put it into the drying oven for 30 minutes at 60 °C. Finally, the sample was being heated in the muffle furnace, at the rate 2 °C/min. The temperature was kept at 500 °C for 2 hours. Let it cool to the room temperature in the stove. We can gain the porous TiO₂ thin film.

For comparison, we also used dip-coating method to plated pure TiO₂ and pure PS on the other two clean FTO glasses. And the TiO₂ film was dried at 500 °C for 2 h, while the PS film was dried at 60 °C for 30 minutes. The porous TiO₂ film including a small amount of residual template, the pure TiO₂ film and the PS film was named as S_{TP}, S_T, S_P, respectively.

Structure and characterization. The structure and morphology of the porous TiO_2 thin film was observed using a KYKY-2800 scanning electron microscopy (SEM). The average particle size of TiO_2 thin film, crystal type and weight percentage were analyzed with a Japan Science D/max-2500/PC using $\text{Cu K}\alpha$ radiation ($\lambda=0.154059$ nm). The Raman features of the samples were detected by an inVia Raman spectrometer with the argon ion gas laser of 514.5 nm wavelength, 20 mW laser powers, 5% attenuation. Surface photovoltage spectroscopy was measured by the multifunctional spectroscopy self-assembled, including the SR830 lock-in amplifier and SBP300 monochromator, scanning wavelength from 300 to 800 nm.

Introduction of SPS and PAS. The signals of SPS and PAS were measured by the multifunctional spectroscopy self-assembled. Testing devices are shown in figure 1.

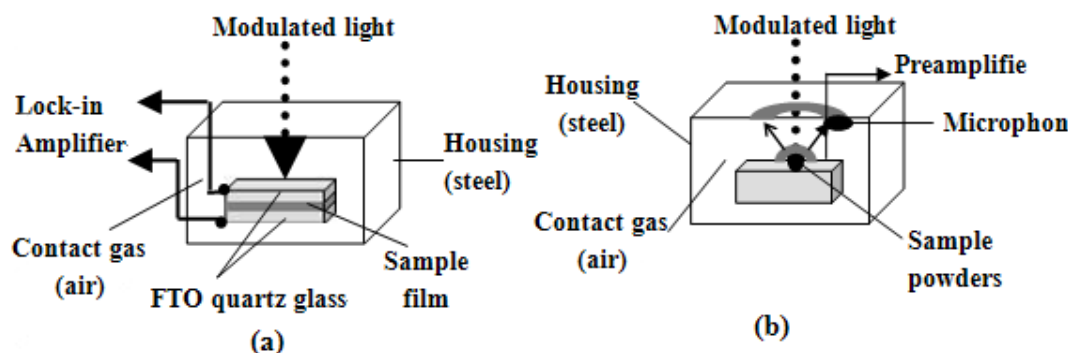


Fig. 1 Sample cells of SPS (a) and PAS (b)

Surface of the photovoltaic effect have been successfully used in the semiconductor surface of a variety of electronic processes. The photovoltage cell is shown as Fig.1 (a). The surface barrier changed, which is due to the photogenerated carriers of the material surface being induced when the incident light acts on the sample side. The surface photovoltage of the sample is the difference of work function between the upside and backside.

The inspection and measurement of PAS was that the sample was in the photoacoustic cell collocated a high sensitivity microphone, as Fig.1 (b). The sample absorbed the given frequency (The frequency was 22 Hz in this experimentation). The sample's photoacoustic signals relate with the nonradiative transition phenomenon coming from the photoinduced carriers in surface space charge region. It results in that the sample and ambient gas produce periodic heat air current under the action of the periodic photostimulation. And it causes the periodic vibration of the sample's crystal lattice. Sound pressure change coming out from the interface between the sample and the ambient gas transmits by the air. It is detected as a format of the acoustic signal by a high sensitivity microphone. Photoacoustic pectroscopy is gained after being treated by preamplifier and lock-in amplifier.

Results and discussion

Microstructure analysis of samples.

Fig. 2 shows SEM image of the sample S_{TP} . It can be seen that the TiO_2 thin film prepared with a template of PS is ordered macroporous structure, the average pore size 580 nm. The pores are hexagonal structure. The dipping and filling process of colloidal crystal template was that the precursor was filled into the interspaces of PS microspheres gradually with the help of capillary force. The PS had removed after being calcined. There is still a small amount of residual template PS from the figure, which damages the integrity of such a similar inverse opal structure pore.

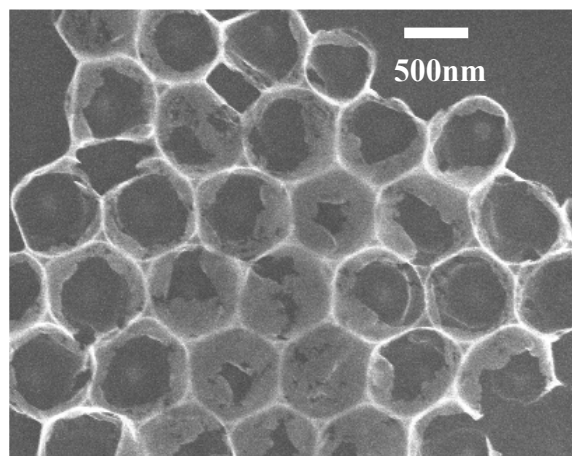


Fig. 2 SEM image of sample S_{TP}

Fig. 3 shows XRD patterns of TiO₂ film and TiO₂ powders. The two samples' main diffractive peaks are narrow and sharp. And the grain growth is more complete and better crystallinity. Phase analysis of samples, we can see the major components of them are anatase. It is found that the diffraction peaks are the obvious diffraction peaks of anatase after being standardized.

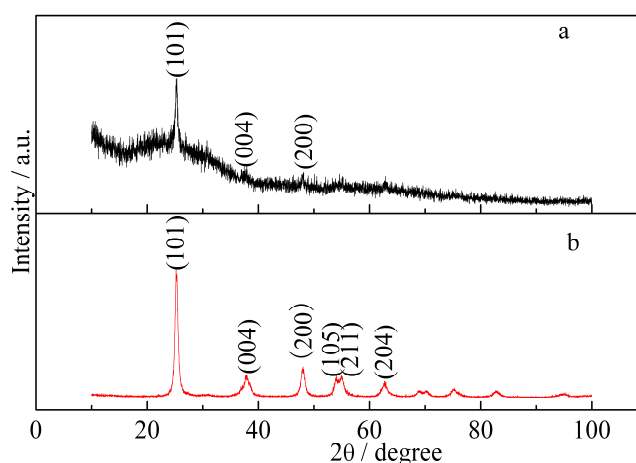


Fig. 3 XRD patterns of TiO₂ film and TiO₂ powders

The Raman spectroscopy experiments were only done on TiO₂ powders for nanocrystalline TiO₂ thin film having the same composition as TiO₂ powders. Fig. 4 shows Raman spectroscopy of TiO₂ powders.

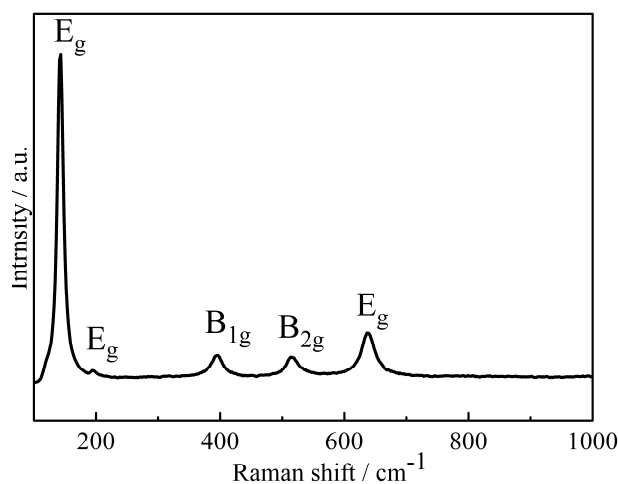


Fig. 4 Laser Raman spectrum of the TiO₂ powders

Raman spectra of TiO_2 powders showed anatase vibration mode. There are obviously five Raman peaks: E_g (145 cm^{-1} (vvs)) is a very strong vibration; E_g (195 cm^{-1} (w)) is a weak vibration; B_{1g} (399 cm^{-1} (m)) is a moderate strong vibration; B_{2g} (513 cm^{-1} (m)) is a moderate strong vibration; E_g (640 cm^{-1} (m)) is a moderate strong vibration [17-18]. Analysis shows that the main composition of the sample is anatase, which is consistent with the analysis of XRD spectrum.

Analysis of photoelectron characteristics

Analysis of SPS. In order to study how the residual template PS influences the SPV characteristics of TiO_2 thin films, Fig. 5 shows the surface photovoltage spectrum of S_{TP} , S_T , S_P thin films.

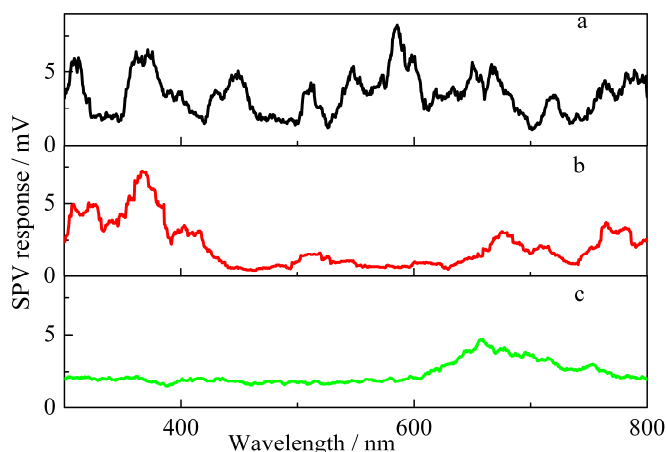


Fig. 5 SPS spectra of thin films S_{TP} (a), S_T (b), S_P (c)

As shown in Fig. 5, The SPV of S_P thin film response is mainly in the long wavelength region 600-750 nm and the main peak is at 657 nm which is $\pi-\pi^*$ electronic transition in benzene ring [19]. The SPV of S_T thin film response is mainly in the short wavelength area 300-400 nm and the main peak is at 367 nm which is the main band gap charge transfer ($O_{2p} \rightarrow Ti_{3d}$) transition of anatase. The SPV of S_{TP} thin film responds from the ultraviolet to the visible light. The peak in 300-400nm is primary from the band-band transition of TiO_2 , the peak in 600-800 nm comes from the $\pi-\pi^*$ electronic transition in benzene ring, while the peak in 400-600nm is the result of the interaction between TiO_2 and the residual template PS. It indicates that the presence of a small amount of template not only broadens the scope of SPV response but also increases the intensity.

Analysis of PAS. Before the measurement of PAS, we need to make the standard energy spectrum of the light as a benchmark. It can eliminate the influence on account of unequal distribution of light energy during processing the data as normalization. Black carbon is generally used as a standard sample. Do its photoacoustic spectra. Fig. 6 shows the PAS of black carbon. It can be seen that there is a strong characteristic peak of Xenon lamps near 365 nm. So it is necessary to do PAS normalization for the samples.

Normalized PAS of TiO_2 powders is shown as Fig. 7. There are PA signals in the region of 400-700 nm. It illuminates that the photoinduced carriers from electronic transition bring SPV effect and the remaining energy release as the form of lattice vibration in the complex process. There are strong peaks at 456 nm and 678 nm, while troughs at 372 nm and 587 nm. Therefore, it suggests a relationship of the complementary energy between PA effect and SPV effect.

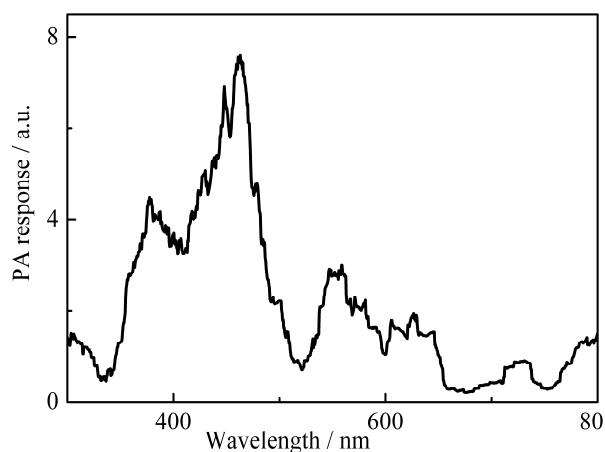
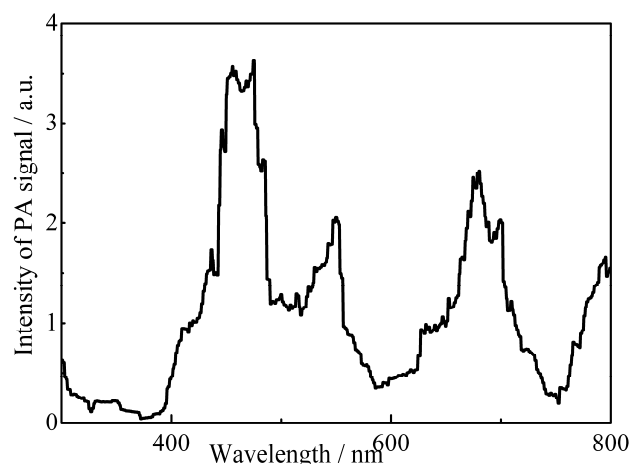


Fig. 6 PAS of black carbon

Fig. 7 Normalized PAS of TiO₂ powders

Conclusions

The macroporous nano-TiO₂ thin film was prepared by a dipping-pulling method, in which PS was used as template, and nano-TiO₂ sol as a precursor. The structure and properties of the films are influenced by a small amount of residual template PS included in the sample. SEM observation shows that the presence of a little residual template impacts the integrity of the holes with the inverse opal structure. The results of the SPS analysis show that the residual template affects specially optoelectronic properties of porous TiO₂ thin film, resulting mainly in broadening of the scope and increasing of the intensity of SPV response. Combined with photoacoustic technique, we have studied the energy complementary relationship between SPV and PA in the process of electron transition.

Acknowledgments

This work is supported by the National Nature Science Foundation of China (No. 20573090), Key Project of Natural Science Foundation of Hebei Provincial Department of Education (No. ZH200814). Fax: +86 335 8057047; Tel: +86 335 8074631.

References

- [1] E. Yablonovitch. Inhibited spontaneous emission in solid state physics and electronics. *Phys. Rev. Lett.* 58 (1987) 2059-2062.
- [2] S. John. Strong localization of photons in certain disordered dielectric superlattices. *Phys. Rev. Lett.* 58 (1987) 2486-2489.
- [3] K.M. Leung, Y.E. Liu. Full Vector wave calculation of photonic band structures in face-centered-cubic dielectric media. *Phys. Rev. Lett.* 65 (1990) 2646-2648.
- [4] E. Yablonovitch. Photonic band-gap structure. *J. Opt. Soc. Am. B* 10 (1993) 285-289.
- [5] T. Quang, M. Woldeyohannes, S. John and G.S. Agarwal. Coherent Control Of Spontaneous Emission near a Photonic Band Edge: A Single-Atom Optical Memory Device. *Phys. Rev. Lett.* 79 (1997) 5238.
- [6] Z.Y. Li, L.L. Lin and Z.Q. Zhang. Spontaneous Emission from Photonic Crystals: Full Vectorial Calculations. *Phys. Rev. Lett.* 84 (2000) 4341.
- [7] E. Yablonovitch, T.J. Gmitter, K.M. Leung, Photonic Band structure: The face-centered-cubic case employing Nonspherical atoms, *Phys. Rev. Lett.* 67 (1991) 2295.

-
- [8] B.O. Regan, M.Gratzel. A low-cost, high-efficiency solar cell based on dyesensitized colloidal TiO₂ films. *Nature* 353 (1991) 737-740.
- [9] E.W. McFarland, K.Tang. A photovoltaic device structure based on internal electron emission. *Nature* 421 (2003) 616-618.
- [10] Wijnhoven, J. E. G. J. & Vos. W. L. Preparation of photonic crystals made of air spheres in titania. *Science* 281 (1998) 802.
- [11] J.C. Knight, P.St.J Russell. *Science* 296 (2002) 276.
- [12] K. Yamada, H. Morita, A.Shinya, M. Notomi. *Opt. Commun*, 198 (2001) 395.
- [13] A. Stein, Sphere templating method for periodic porous solids. *Microporous and Mesoporous Materials*. 44 (2001) 227-239.
- [14] B.T. Holland, C.F. Blandford, A. Stein. Synthesis of highly ordered three dimensional macroporous structure of amorphous or crystalline inorganic oxides, phosphate, and hybrid composites. *Chem. Mater* 11 (1999) 795-805.
- [15] H. Yah, C.F. Blandford, B.T. Holland, et al. General synthesis of periodic macroporous solids by templated salt precipitation and chemical conversion. *Chem. Mater* 12 (2000) 1134.
- [16] J. S. Yin and Z. L. Wang. Template-assisted self-assembly and cobalt doping of ordered mesoporous titanium nano structures. *Adv. Mater* 11 (1999) 469.
- [17] J.G. Traylor and H.G. Smith. Lattice Dynamics of Rutile. *Phys.Rev. B* 13 (1971) 3457.
- [18] J.C. Parker and R.W. Siegel. Calibration of the Raman Spectrum to the Oxygen Stoichiometry of Nanophase TiO₂. *Appl.Phys.Lett.* 9 (1990) 943.
- [19] Xing-ling Chang, The Color and Conjugation π - π^* Transition of Organic Compound, *Adv. Mater. Sci. Eng.* Vol. 21 (2001).

A simple texturization approach for mono-crystalline silicon solar cell with low TMAH concentration solution

OU Weiying^{1,2}, ZHANG Yao¹, LI Hailing¹, ZHAO Lei¹, ZHOU Chunlan¹,
DIAO Hongwei¹, LIU Min¹, LU Weiming¹, ZHANG Jun¹, WANG Wenjing^{1, a}

¹Key Laboratory of Solar Thermal Energy and Photovoltaic System, Institute of Electrical Engineering, The Chinese Academy of Sciences, No.6 Beiertiao Zhongguancun, Haidian District, Beijing 100190, China

²Department of Electronic Engineering, Guilin University of Electronic Technology, Guilin 541004, China

^aemail: wjwangwj@126.com

Keywords: TMAH; texture; pyramids.

Abstract. Texturing for mono-crystalline silicon solar cell by chemical anisotropic etching is one of the most important techniques in photovoltaic industry. In recent years, tetramethylammonium hydroxide (TMAH) solution or a mixture of TMAH solution with IPA was reported to be used for random pyramids texturization on silicon surface due to its non-volatile, nontoxic, good anisotropic etching characteristics and uncontaminated metal ions. However, most of the studies were reported about the etching processes by using high TMAH concentration solutions. In this study, a simple and cost-effective approach for texturing mono-crystalline silicon wafers in low TMAH concentration solutions was proposed. Etching was performed on (100) silicon wafers using silicon-dissolved tetramethylammonium hydroxide (TMAH) solutions (0.5~1 %) without addition of surfactant. The surface phenomena, surface morphology and surface reflectance have been analyzed. A textured surface with smaller and smooth pyramids can be realized by using 1 % silicon-dissolved TMAH solutions.

Introduction

Anisotropic texturization of mono-crystalline silicon wafers to form random pyramids is one of the important techniques in modern solar cell processing [1,2]. Currently, a mixture of Potassium hydroxide (KOH) or sodium hydroxide (NaOH) and isopropyl alcohol (IPA) is the most common etchant in photovoltaic production. The addition of IPA can improve the wettability of silicon surface and remove hydrogen bubbles sticking on the silicon wafers, finally lead to a uniformity of pyramids [3]. However, IPA is volatile in a heated etching bath because the boiling point of IPA is around 82°C. Therefore, IPA must be constantly added to the solution during the etching process, which results in a difficult control and high consumption of IPA. The high consumption of IPA can be the main overall cost in current commercial texturing technology. In addition, KOH and NaOH etching solutions are cost and time efficient but result in the potassium and sodium ion contaminations to the solar cell devices. In order to reduce the cost of silicon texturization, some new methods have been reported [4,5]. However, most of the etchants of these new methods also resulted in metal ion contamination.

In recent years, tetramethylammonium hydroxide (TMAH) solution was reported to be used for random pyramids texturization on silicon surface due to its non-volatile, nontoxic and good anisotropic etching characteristics [6-8]. Most importantly, TMAH solution presents uncontaminated metal ions. However, all of these texturization processing techniques were reported using high TMAH concentration solution and resulting in high cost of texturization processes because TMAH is expensive.

In this paper, a simple and low-cost silicon texturization approach is proposed. The texturing processes on silicon wafers with silicon-dissolved TMAH solutions without addition of surfactant have been studied. Experiments were carried out in very low TMAH concentration solutions at 95 °C

for different etching time. Detailed analyses of the surface phenomena, etched rates, surface morphology and surface reflectance have been given.

Experimental conditions

In this study, P-type CZ wafers with {100} orientation, 200 μm thick and 0.5-3 $\Omega\cdot\text{cm}$ resistivity were used. The wafers were cut into 2 cm $\times$ 1.5 cm samples without any clean process. The samples were hold in a quartz basket. Silicon-dissolved TMAH solutions were realized by dissolving a certain amount of silicon in 10 wt.% commercial TMAH solution. The solutions with different TMAH concentration were prepared by diluting the silicon-dissolved TMAH solutions with deionized water (DIW). Experiments were carried out in a Thermostatic Bath covered with a glass vessel in order to limit evaporation of the water. The main technical datum of the thermostatic bath are: temperature fluctuation $\leq \pm 0.05^\circ\text{C}$, horizontal temperature uniformity $\leq \pm 0.05^\circ\text{C}$, vertical temperature uniformity $\leq \pm 0.1^\circ\text{C}$. The temperatures of the thermostatic bath were maintained at 80°C . The etching solution was hold in a glass beaker covered with a glass vessel in order to reduce the loss of the solutions by evaporation. Firstly, the beaker was put in the thermostatic bath, and then the quartz basket was immersed into the beaker after the temperatures of the thermostatic bath maintaining stabilization. Specially, an agitation of the basket for about 30 seconds was necessary in order to achieve a uniform wettability of the silicon surface. The etching time was ranging from 10 min to 30 min. After the etching process, the samples were taken out and ringed in pure DI water. Finally, the samples were dried in air for about 10 min.

The surface morphology of the silicon wafers was analyzed by a Scanning Electron Microscope (SEM). The surface reflectance in the 350-1100nm range was measured using UV-VIS-NIR spectrophotometer.

Results and discussion

Fig. 1 shows the SEM pictures of silicon surface textured with 1 % TMAH solution at 95°C for etching time ranging from 10 min to 30 min. During the texturization processes, no hydrogen bubbles were found to adhere to the samples surface in this condition. It can be found from Fig. 1(a) that the density of the pyramids was very high and the sizes of pyramids were small after etching for 10 min. The size of the pyramids increased as the etching time increased. However, the density of the pyramids decreased simultaneously. Some of the pyramid structures were found to collapse when etched for 30 min. The experimental results indicate that an appropriate etching time is necessary in order to texture mono-crystalline silicon in this condition.

Compare to the 1 % TMAH solutions, decreasing the concentration of TMAH the surface morphology of the samples changes dramatically, as shown in Fig. 2. Very few hydrogen bubbles were found to adhere to the samples surface in this condition. Poor surface coverage with a damaged layer was obtained for an etching time of 15 min. As the etching time increased, the damaged layer disappeared. In addition, the density of the pyramids increased simultaneously for etching time range from 20 min to 25 min. However, for an etching time of 30 min, some of the pyramid structures were found to collapse. From the pictures, it can be seen that a textured surface with smaller and smooth pyramids was obtained even etching in the solution with very low TMAH concentration.

The experimental results let us suggest that not only the etchants but also the etching temperature all have an important effect on etching behaviors. The commonly accepted model for description of silicon etching process includes 5 stages [8]: (1) Diffusion of reagent particles towards silicon surface. (2) Adsorption of reactive and non-reactive particles (ions) on silicon surface. (3) Oxidation and chelating reactions of silicon surface. (4) Desorption of reaction products. (5) Diffusion of reaction products from silicon surface to the bulk of silicon. In the silicon-dissolved TMAH solutions, TMA^+ , $\text{SiO}_2(\text{OH})_2^{2-}$, OH^- and H_2O coexist, and all of these components can diffusion toward silicon surface and then be adsorbed on silicon surface.

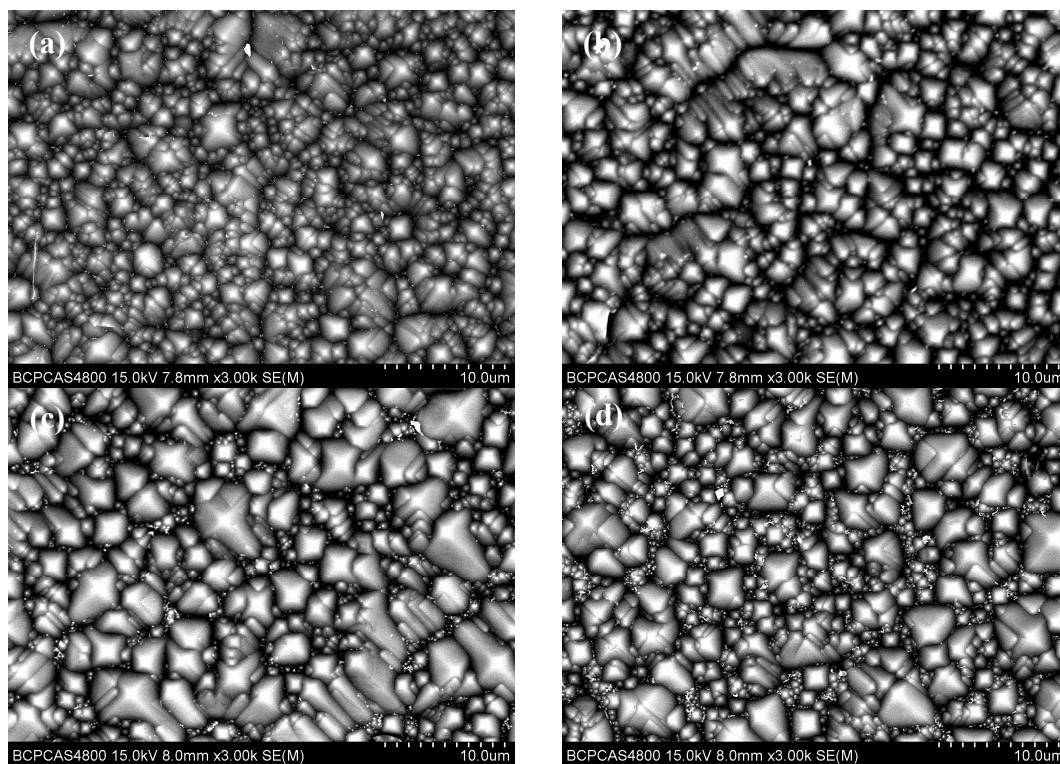


Fig. 1. SEM pictures of surface morphology on texturing mono-crystalline silicon in 1 % TMAH solutions at temperature 95°C. (a)10 min. (b)15 min. (c)25 min. (d)30 min.

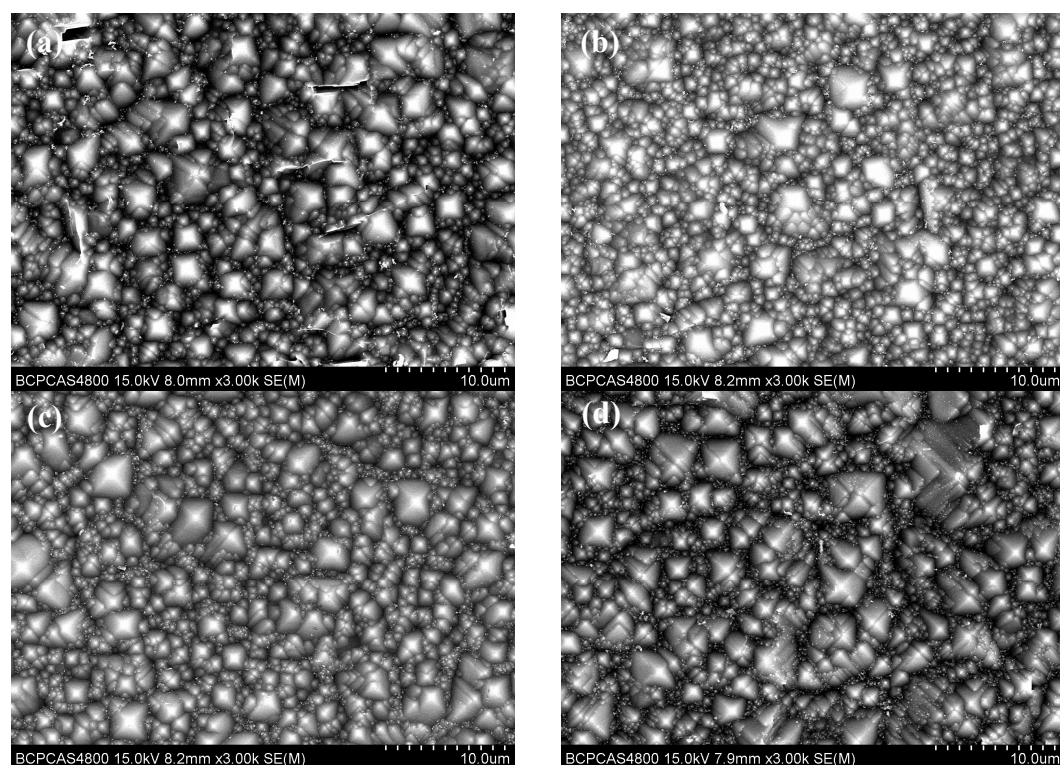


Fig. 2. SEM pictures of surface morphology on texturing mono-crystalline silicon in 0.5 % TMAH solutions at temperature 95°C. (a) 15 min. (b) 20 min. (c) 25 min. (d) 30 min.

In the initial stages of experiment, $\text{TMA}^+/\text{SiO}_2(\text{OH})_2^{2-}$ components are most prone to be adsorbed as a mask because their higher concentration in silicon-dissolved TMAH solutions. However, as the etching time increases, more and more $\text{OH}^-/\text{H}_2\text{O}$ were adsorbed on the etching surface because the

diffusion $\text{OH}^-/\text{H}_2\text{O}$ were fast than that of $\text{TMA}^+/\text{SiO}_2(\text{OH})_2^{2-}$ in high etching temperature. When the etching time is long enough, some of the pyramid structures collapse because the fast of oxidation with large amount of $\text{OH}^-/\text{H}_2\text{O}$ adhering on the etching surface. In addition, we also assume that hydrogen bubbles might easily leave the samples surfaces due to high etching temperature.

Fig. 3 shows the reflectance of resulted surfaces textured under different conditions. Comparing to the surface without texturization, the reflectance of untextured silicon wafer is very high. For samples textured in 0.5 vol. % TMAH solution for 20 min, the reflectance was higher because pyramids were smaller. However, the reflectance was found to decrease with the increase of etching time up to 25 min. For samples etched in 0.5 % for 20 min and 1 % for 10 min, the reflectance was almost the same but still showed a little higher than the sample etching in 1% TMAH for 15 min. The lowest reflectance has been observed in 1 % TMAH concentration solution when etched for 15 min due to the larger sizes of pyramids. It indicates that the decrease of reflectance is obvious by using very low TMAH concentration solution to etch silicon wafers.

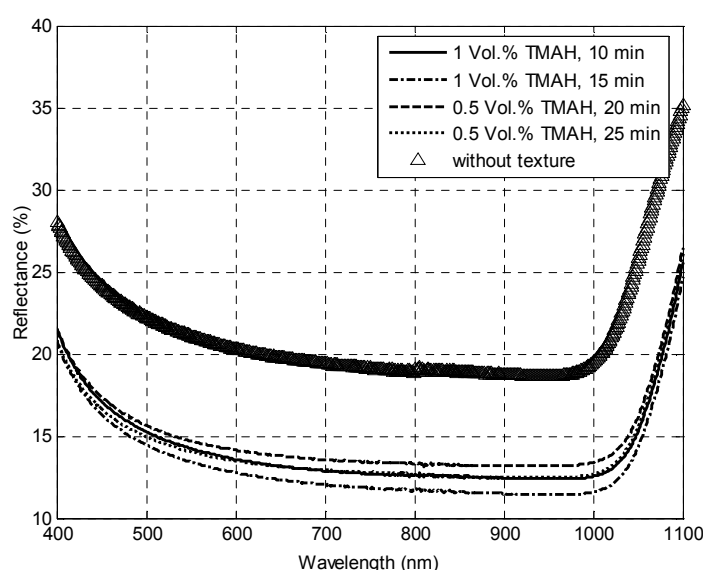


Fig. 3. The textured surface reflectance versus wavelength at 95°C under different texturing conditions.

Summary

In this study, we proposed a simple and cost-effective approach for texturing crystalline silicon wafers by using very low TMAH concentration solutions. Etching experiments were performed on (100) silicon wafers by using silicon-dissolved TMAH solutions without any other surfactant at high etching temperature. Basing on experimental results and theoretical explanations, it is assumed that the etchants and the etching temperature had an important effect on etching processes. The diffusion $\text{OH}^-/\text{H}_2\text{O}$ was faster than that of $\text{TMA}^+/\text{SiO}_2(\text{OH})_2^{2-}$ in high etching temperature and resulted in fast oxidation reaction. It also suggests that hydrogen bubbles might easily leave the samples surfaces due to high etching temperature. A textured surface with small and smooth pyramids can be realized even in the condition of very low silicon-dissolved TMAH concentration solution (0.5 % in this case) at 95°C for 20 min to 25 min.

Acknowledgment

This work was supported by the Knowledge Innovation Program of the Chinese Academy of Sciences Grant No.KGCX2-YW-382.

References

- [1] P. Campbell, M.A. Green: J. Appl. Phys Vol. 62 (1987), p. 243.
- [2] J.M. Rodriguez, I. Tobias, A. Luque: Solar Energy Materials & Solar Cells Vol. 45 (1997), p. 241.
- [3] U. Gangopadhyay, K. Kim, S.K. Dhungel, P.K. Basu, J. Yi: Renewable Energy Vol. 31 (2006), p. 1906.
- [4] U. Gangopadhyay, K. Kim, A. Kandol, J. Yi, H. Saha: Solar Energy Materials & Solar Cells Vol. 90 (2006), p. 3094.
- [5] A.K. Chu, J.S. Wang, Z.Y. Tsai, C.K. Lee: Solar Energy Materials & Solar Cells Vol. 93 (2009), p. 1276.
- [6] P. Papet, O. Nichiporuk, A. Kaminski, Y. Rozier, J. Kraiem, J. F. Lelievre, A. Chaumartin, A. Fave, M. Lemiti: Solar Energy Materials & Solar Cells Vol. 90 (2006), p. 2319.
- [7] O. Tabata: Sensors and Actuators A Vol. 53 (1996), p. 335.
- [8] I. Zubel, M. Kramkowska: Sensors and Actuators A Vol. 93 (2001), p. 138.

Effects of IPA on texturing process for mono-crystalline silicon solar cell in TMAH solution

OU Weiyang^{1, 2}, ZHANG Yao¹, LI Hailing¹, ZHAO Lei¹, ZHOU Chunlan¹,
DIAO Hongwei¹, LIU Min¹, LU Weiming¹, ZHANG Jun¹ and WANG Wenjing^{1,a}

¹Key Laboratory of Solar Thermal Energy and Photovoltaic System, Institute of Electrical Engineering, The Chinese Academy of Sciences, Beijing 100190, China

²Department of Electronic Engineering, Guilin University of Electronic Technology, Guilin 541004, China

^aEmail: wjwangwj@126.com

Keywords: Texture; pyramids; TMAH; IPA.

Abstract. Texturization of mono-crystalline by chemical anisotropic etching is one of the most important technologies for modern silicon photovoltaic. IPA is usually added to the alkaline etchants to improve the uniformity of the random pyramid texture due to remove hydrogen bubbles sticking on the silicon wafer by improving the wettability of wafer surface. In this investigation, we carried out a systematic study on the influence of IPA concentrations on the textured surface. The etching experiments were performed on (100) silicon wafer in a mixture of 20 vol. % commercial TMAH solutions (10 wt.%) and IPA (rang from 0~12 vol. %) for etching time ranging from 10 to 70 min at 80°C. The etching mechanism in the TMAH solutions with IPA addition was explained basing on the experimental results and the theoretical considerations.

Introduction

The random texturing of mono-crystalline silicon solar cells is a key technology used to improve the conversion efficiency by increasing the amount of light absorption [1,2]. Usually, a textured surface with uniform, smaller and smooth pyramids are always preferred for the commercial screen-printed solar cell because metal coverage in the finger lines of the cell is better [3-5]. Additionally, a textured surface without bubble spots is very important in the solar cell industries because a wafer with bubble spots on the surface is not interested by the purchasers. In modern solar cell processing, the most conventional anisotropic etching solution is aqueous potassium hydroxide (KOH) and sodium hydroxide (NaOH) solutions. KOH and NaOH etching solutions are cost and time efficient but result in the potassium and sodium ion contaminations to the solar cell devices [6]. Tetramethylammonium hydroxide (TMAH, $(\text{CH}_3)_4\text{NOH}$) is a well-known etchant solution widely used in microelectronics due to its no alkali ions, non-volatile, nontoxic and good anisotropic etching characteristics[7-9]. Since You et al [10] firstly reported on the use of TMAH solution in anisotropic etching to obtain random pyramidal silicon texturing, many investigations have been carried out into the use of TMAH solution to create uniform and reproducible pyramidal in recent year [6,11].

Generally, Isopropyl (IPA) is added to alkaline etchants to improve the uniformity of the random pyramid texture. In spite of some explanations of IPA effect on texturing processing by improving the wettability of wafer surface and then removing hydrogen bubbles sticking on the silicon wafer, its role in the texturing processes has not been fully understood. Additionally, few studies focused on the amount of IPA ensuring the improvement of surface morphology in the etching processing.

In this work, we investigated the texturing processes of mono-crystalline silicon with (100) crystallographic orientation by using a mixture of 20 vol. % commercial TMAH solutions (10 wt.%) and IPA (rang from 0~12 vol. %) for etching time ranging from 10 to 70 min at 80°C. Specially, we focused on the analysis of the etching mechanism in the TMAH solutions with IPA addition based on the experimental results and the theoretical considerations.

Experimental

In this study, P-type CZ wafers with {100} orientation, 200 μm thick and 0.5-3 $\Omega\text{-cm}$ resistivity were used. The wafers were cut into 2 cm $\times$ 1.5 cm samples without any clean process. The samples were hold in a quartz basket. The etchant solutions were prepared using a mixture of commercial TMAH solution (10 wt.%), deionized (DI) water and IPA, and the composition of the mixture is shown in table 1. Experiments were carried out in a Thermostatic Bath covered with a glass vessel in order to limit evaporation of the water. The main technical datum of the thermostatic bath are: temperature fluctuation: $\leq \pm 0.05^\circ\text{C}$, horizontal temperature uniformity: $\leq \pm 0.05^\circ\text{C}$, vertical temperature uniformity: $\leq \pm 0.1^\circ\text{C}$. The temperatures of the thermostatic bath were maintained at 80°C . The etching solution was hold in a glass beaker covered with a glass vessel. In order to reduce the loss of IPA by evaporation, the glass beaker was put into the thermostatic bath firstly, and then IPA was added after the temperatures were maintained at 80°C . Lastly, the quartz basket with samples was immersed in the etching solution after the temperatures of the thermostatic bath maintaining stabilization again. Specially, an agitation of the basket for about 30 seconds was necessary in order to achieve a uniform wettability of the silicon surface. The etching time was ranging from 10 min to 35 min. After the etching processes, the samples were taken out and ringed in pure DI water. Finally, the samples were dried in air for about 10 min.

The surface morphology of the silicon wafers was analyzed firstly by an optical microscope and then a Scanning Electron Microscope (SEM) was used to analyze the surface in detail. To characterize the optical performance, a UV-VIS-NIR spectrophotometer was used to measure the surface reflectance with light in the wavelength range from 350 to 1100 nm at near normal incidence.

Table 1 Experimental conditions and surface phenomena of the resulted samples

Batch No.	10 wt.% commercial TMAH solution /DI /IPA concentration [vol.%]	Quantity of samples	Etching time [min]	Surface phenomena
1	20/80/0	3	20, 30 , 35	large amount of bubble spots, present damaged layer.
2	20/78/2	3	15, 20, 35	few bubble spots, Present damaged layer after etching 15 min.
3	20/75/5	6	10-35	no bubble spot, Present damaged layer for etching time ranging from 10 to 15 min.
4	20/74/6	6	10-35	Without bubble spot, Present damaged layer for etching time ranging from 10 to 15 min.
5	20/72/8	6	10-35	Without bubble spot, present damaged layer for etching time ranging from 10 to 20 min.
6	20/68/12	2	30, 70	without bubble spot, Present surface passivation even after etching for 70 min.

The surface phenomena of etched surface are shown in Table 1. It is observed that large amount of bubble spots were observed etched in the solution without addition of IPA. With the increase of IPA concentrations, bubble spots disappeared. However, the textured surfaces coverage with a passivation layer was observed etched in the solution with very high IPA concentrations even for a long etching time.

Fig.1 shows the SEM picture of the silicon wafer textured in 20 vol.% TMAH solutions without addition of IPA for 30 min. Poor surface coverage with a damaged layer was obtained. When IPA was

added to the solution, the qualities of surface increased. Fig.2 shows the SEM pictures of surface morphology of the silicon wafers etched in the solutions with a wide range of IPA concentrations at 80°C for 30 min. As shown in Fig.2, the surface coverage of pyramid structures improves significantly after addition of IPA. The size of pyramids decreased with increase IPA concentrations. In addition, for very high IPA concentrations, exceeding 8 vol. %, the uniformity of the size of the pyramids was found decreased. Uniform texturization throughout the silicon surface was achieved etched in 20 vol.% TMAH solutions with addition of 6 vol.% IPA. The obtained results showed that the amount of IPA which ensures good surface quality after the etching processes is close to 6 vol.%.

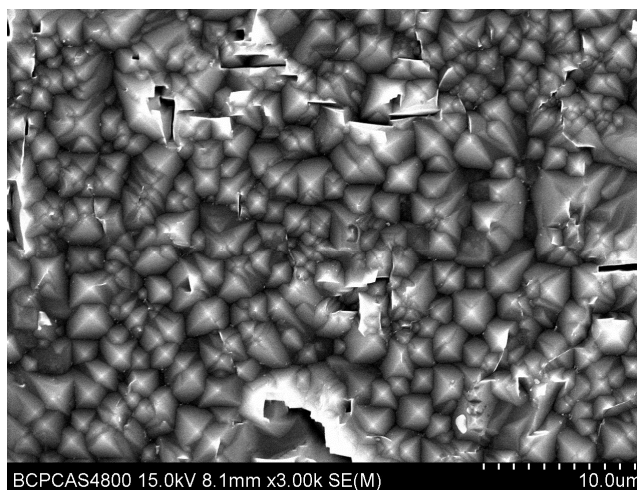


Fig.1 SEM picture of surface morphology on textured mono-crystalline silicon etched in 20 vol. % commercial TMAH solution (10 wt.%) at temperature 80°C for 30 min

The etching time dependence for the etched surface etched in a mixture solution of 20 vol.% TMAH solution (10 wt.%) with addition of 6 vol.% IPA at 80°C for etching time ranging from 10 min to 35 min are shown in Fig.3. Fig.3(a) and (b) show that a damaged layer still presented for etching time smaller than 15 min. As time increased, the damaged layer disappeared, and the surface coverage of pyramid structures improves significantly. The surface morphologies of the etched wafers are almost the same for etching time ranging from 25 to 35 min. This means that a stable surface quality can be achieved etched in 20 vol.% TMAH solution (10 wt.%) with addition of 6 vol.% IPA for a wide range etching time.

The influence of the IPA concentrations to the reflectance of the silicon surfaces is shown in Fig.4. The reflectance decreased with increase IPA concentrations up to 5 vol.%. For lower IPA concentrations, the reflectance was higher. The highest reflectance has been observed without IPA addition due to the presence of a damaged layer in the resulted surface. The lowest reflectance was found in the sample etched in 6 vol.% IPA+ 20 vol.% TMAH solution. The results are explained by uniformity improvement. Fig.5 shows the influence of etching time to the reflectance of the sample etched in 6 vol.% IPA+ 20 vol.% TMAH solution at 80°C. The reflectance was found to decrease with increasing etching time up to 20 min because of the disappearance of the damaged layers. For 25 to 35 min, the reflectance was lowest because the etched wafers were covered with uniform pyramids. This means that a good and stable quality etching surface with low reflectance can be achieved in 6 vol.% IPA +20 vol. TMAH for a wide range etching time which will be good for the industry.

It has been approved that etching process carried out in the medium IPA concentrations solutions (6 vol.% IPA in our case) results in a good surface quality with uniform pyramids and lowest surface reflectance. Poor surface quality was obtained in both lower and extreme high IPA concentrations. In order to explain the etching mechanism, some theoretical studies should be carried out.