

Preparation and application of Wideband Gap Nanocrystalline Semiconductors Thin Films

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ABSTRACT

Transparent conducting Al-doped ZnO (AZO) thin films have been deposited by sol-gel route. Starting from an aqueous solution of zinc acetate by adding aluminum chloride as dopant, a c-axis oriented polycrystalline ZnO thin film 100nm in thickness could be spin-coated on glass substrates via a two-step annealing process under reducing atmosphere. The effects of thermal annealing and dopant concentration on the structural, electrical and optical properties of AZO thin films were investigated. The post-treated AZO films exhibited a homogenous dense microstructure with grain sizes less than 10nm as characterized by SEM photographs. The annealing atmosphere has prominent impact on the crystallinity of the films which will in turn influence the electrical conductivity. By varying the doping concentrations, the optical and electrical properties could be further adjusted. An optimal doping concentration of Al/Zn=2.25 at.% was obtained with minimum resistivity of 9.90×10^{-3} ohm-cm whereas the carrier concentration and mobility was 1.25×10^{20} cm⁻³ and 5.04 cm²V⁻¹S⁻¹, respectively. In this case, the optical transmittance in the visible region is over 90%. In addition, photocatalytic removal of indoor level of toluene in the gas phase was performed in a tubular reactor by TiO₂-based photocatalysts under illumination of UV and visible light, respectively. Two types of TiO₂ suspensions were employed in the whole experiments: one prepared by a sol-gel route (designated as SG-TiO₂) and the other by applying a commercial Degussa P25 TiO₂ (designated as P25-TiO₂). All photocatalysts were dip-coated on the inner surface of a Pyrex glass tube and followed by a post-annealing process. For visible-type photocatalysts, the above TiO₂ films were sensitized by tetrakis (4-carboxyphenyl) porphyrin (TCPP) and designated as TCPP/SG-TiO₂ and TCPP/P25-TiO₂, respectively. The photocatalytic destruction of gaseous toluene by the four catalysts was evaluated. For the UV-type photocatalysts, toluene was decomposed significantly by both types of TiO₂ films at lower toluene concentrations, [T] o. However, the overall removal efficiency (RE) was decreased dramatically as the initial concentration of was elevated to 6.5 ppm for P25-TiO₂ and 4.0ppm for P25-TiO₂, respectively. A plot of toluene elimination capacity (EC) vs. toluene loading rate indicated that the limiting EC for the SG-TiO₂ and P25-TiO₂ was 4.9 and 2.7 mg hr⁻¹ m⁻², respectively. In contrast, either type of dye-sensitized TiO₂ photocatalysts evaluated under illumination of visible light showed relatively low toluene RE as compared to the UV-type photocatalysts under identical conditions. After pre-soaking in HCl solution, the activity of the acid-pretreated TCPP/P25-TiO₂ [designated as TCPP/P25-TiO₂ (ACT)] was improved considerably under the identical conditions. The kinetics of photocatalytic decomposition of gaseous toluene in our study generally would follow the Langmuir-Hinshelwood (L-H) model. The rate constant k, as fitted by L-H model, for the SG-TiO₂ based catalysts is larger than that of P25-TiO₂ based catalysts while the absorption constant K, on the contrary, follows the different trend. The higher activity of SG-TiO₂ could be attributed to the smaller grain size (4.6~8.1 nm) of anatase crystals as evaluated in XRD diffraction pattern.

Keywords : AZO、 thin film、 precursor chemistry、 aqueous phase deposition、 Indoor air、 Photocatalytic、 Dye-sensitized TiO₂、 Toluene、 Visible light、 porphyrin.

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REFERENCES

- [1] S. Major, S. Kumar, M. Bhatnagar, K.L. Chopra, *Appl. Phys. Lett.* 49 (1986) 394.
- [2] W.T. Yen, Y. C. Lin, P.C. Yao, J.H. Ke, Y.L. Chen, *Thin Solid Films* 518 (2010) 3882.
- [3] T. Minami, H. Nanto, S. Takata, *Jpn. J. Appl. Sci.* 23 (1984) L280.
- [4] D.R. Sahu, S.Y. Lin, J.L. Huang, *Appl. Surf. Sci.* 253 (2007) 4886.
- [5] H. Kim, A. Pique, J.S. Horwitz, H. Murata, Z.H. Kafafi, C.M. Gilmore, D.B. Chrisey, *Thin Solid Films* 377-378 (2009) 798.
- [6] M A Kaid, A. Ashour, *Appl. Surf. Sci.* 253 (2007) 3029.
- [7] A.F. Aktaruzzaman, G.L. Sharma, L.K. Malhotra, *Thin Solid Films* 198 (1991) 647.
- [8] T. Minami, H. Sonohara, S. Takata, H. Sato, *Jpn. J. Appl. Sci.* 33 (1994) L743.
- [9] W. Tang, D.C. Cameron, *Thin Solid Films* 238 (1994) 83.
- [10] T. Tsuchiya, T. Emoto, T. Sei, *J. Non-Crystal. Solids* 178 (1994) 327.
- [11] M. Ohyama, H. Kozuka, T. Yoko, *J. Am. Ceram. Soc.* 81 (1998) 1622.
- [12] A.E. Jimenez-Gonzalez, J.A.S. Urueta, R. Suarez-Parra, *J. Cryst. Growth* 192 (1998) 430.
- [13] P. Sagar, M. Kumar, R.M. Mehra, *Thin Solid Films* 489 (2005) 94.
- [14] T. Schuler, M.A. Aegerter, *Thin Solid Films* 351 (1999) 125 [15] S.Y. Kuo, W.C. Chen, F.I. Lai, C.P. Cheng, H.C. Kuo, S.C. Wang, W.F. Hsieh, *J. Crystal Growth* 287 (2006) 78.
- [16] J.H. Lee, K.H. Ko, B.O. Park, *J. Crystal Growth* 247 (2003) 119.
- [17] Y.S. Kim, W.P. Tai, *Appl. Surf. Sci.* 253 (2007) 4911 [18] V. Musat, B. Teixeira, E. Fortunato, R.C.C. Monteiro, P. Vilarinho, *Surf. Coat. Technol.* 180-181 (2004) 659.
- [19] Z. Xu, H. Deng, J. Xie, Y. Li, Y. Li, *J. Sol-Gel Sci.* 36 (2005) 223.
- [20] H. Van den Rul, D. Mondelaers, M.K. Van Bael, J. Mullens, *J. Sol-Gel Sci.* 39 (2006) 41.
- [21] D. Mondelaers, G. Vanholyland, H.V. Rul, J. D' Haen, M.K. Van Bael, J. Mullens, *MRS Bull.* 37 (2002) 901.
- [22] K. Van Werde, D. Mondelaers, G. Vanholyland, D. Nelis, M.K. Van Bael, J. Mullens, L.C. Van Poucke, *J. Mater. Sci.* 37 (2002) 81.
- [23] D. Mondelaers, G. Vanholyland, H. Van den Rul, J. D' Haen, M.K. Van Bael, J. Mullens, L.C. Van Poucke, *J. Sol-Gel Sci.* 26 (2003) 523.
- [24] Y.G. Wang, S.P. Lau, X.H. Zhang, H.H. Hng, H.W. Lee, S.F. Yu, B.K. Tay, *J. Non-Crystal. Solids* 259 (2003) 335.
- [25] S.W. Xue, X.T. Zu, W.G. Zheng, M.Y. Chen, X. Xiang, *Physica B* 382 (2006) 201.
- [26] K.E. Lee, M.S. Wang, E.J. Kim, S.H. Hahn, *Current Appl. Phys.* 9 (2009) 683.
- [27] S. Cho, J. Ma, Y. Kim, Y. Sun, G.K.L. Wong, J.B. Ketterson, *Appl. Phys. Lett.* 75 (1999) 2761.
- [28] Y. Igasaki, H. Saito, *Thin Solid Films* 199 (1991) 223.
- [29] A.A. Ogwu, E Bouquerel, O Ademosu, S Moh, E Crossan, F Placido, *J. Phys. D: Appl. Phys.* 38 (2005) 266.
- [30] M. Hilgendorff, L Spanhel, Ch. Rothenhousler, G. Muller, *J. Electrochem. Soc.* 145 (1998) 3632.

- [31] K.H. Kim, K.C. Park, D.Y. Ma, *J. Appl. Phys.* 81 (1997) 7764.
- [32] M. Berber, V. Bulto, R. Klis, H. Hahn, *Scripta Materialia* 53 (2005) 547.
- [33] R.F. Silva, E.D. M.E.D. Zaniquelli, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 198 – 200 (2002) 551.
- [34] K.N.P. Kumar, K. Keizer, A.J. Burggraaf, T. Okubo, H. Nagamoto, S. Morooka, *Nature* 358 (1992) 48.
- [35] A.Y. Oral, Z.B. Bahsi, M.H. Aslan, *Appl. Surf. Sci.* 253 (2007) 4593.
- [36] D. Bao, H. Gu, A. Kuang, *Thin Solid Films* 312 (1998) 37.
- [37] P.B. Barna, M. Adamik, *Thin Solid Films* 317 (1998) 27.
- [38] Y.F. Sun, W.F. Liu, Z.D. He, S.L. Liu, Z.Z. Yia, G.T. Du, *Vacuum* 80 (2006) 981.
- [39] Abe R., K. Sayam, and H. Arakaw, "Efficient Hydrogen Evolution from Aqueous Mixture of I- and Acetonitrile Using a Merocyanine Dye-sensitized Pt/TiO₂ Photocatalyst under Visible Light Irradiation," *Chem. Phys. Lett.*, 362, 441 (2002).
- [40] Alberici, R. and W. Jardim, "Photocatalytic Destruction of VOCs in the Gas-phase Using Titanium Dioxide," *Appl. Catal. B: Environ.*, 14, 55 (1997).
- [41] Anderson, C. and A. J. Bard, "An Improved Photocatalyst of TiO₂ /SiO₂ Prepared by a Sol-Gel Synthesis," *J. Phys. Chem.*, 99, 9882 (1995).
- [42] Andersen, I., G. R. Lundqvist, and L. Molhave, "Human Response to Controlled Levels of Toluene in Six-hour Exposures," *Scandinavian J. Work, Envir. & Health.*, 9, 405 (1983).
- [43] Anpo, M. and M. Takeuchi, "The Design and Development of Highly Reactive Titanium Oxide Photocatalysts Operating under Visible Light Irradiation," *J. Catal.*, 216, 505 (2003).
- [44] Argazzi, R., N.Y.M. Iha, H. Zabri, F. Odobel, and C. A. Bignozzi, "Design of Molecular Dyes for Application in Photoelectrochemical and Electrochromic Devices Based on Nanocrystalline Metal Oxide Semiconductors," *Coord. Chem. Rev.*, 248, 1299 (2004).
- [45] Barraud, E., F. Bosc, D. Edwards, N. Keller, and V. Keller, "Gas Phase Photocatalytic Removal of Toluene Effluents on Sulfated Titania," *J. Catal.*, 235, 318 (2005).
- [46] Bischoff, B.L. and M. A. Anderson, "Peptization Process in the Sol-Gel Preparation of Porous Anatase (TiO₂)," *Chem. Mater.*, 7, 1772 (1995).
- [47] Bouzaza, A. and A. Laplanche, "Photocatalytic Degradation of Toluene in the Gas Phase: Comparative Study of Some TiO₂ Supports," *J. Photochem. Photobiol. A: Chem.*, 150, 207 (2002).
- [48] Bouzaza, A., C. Vallet, and A. Laplanche, "Photocatalytic Degradation of Some VOCs in the Gas Phase using an Annular Flow Reactor: Determination of the Contribution of Mass Transfer and Chemical Reaction Steps in the Photodegradation Process," *J. Photochem. Photobiol. A: Chem.*, 177, 212 (2006).
- [49] Campbell, W.M., A. K. Burrell, D. L. Officer, and K. W. Jolley, "Porphyrins as Light Harvesters in the Dye-sensitized TiO₂ Solar Cell," *Coord. Chem. Rev.*, 248, 1363 (2004).
- [50] Carp, O., C. L. Huisman, and A. Reller, "Photoinduced Reactivity of Titanium Dioxide," *Prog. in Solid State Chem.* 32, 33 (2004).
- [51] Chao, C.Y.H., C. W. Kwong, and K. S. Hui, "Potential Use of a Combined Ozone and Zeolite System for Gaseous Toluene Elimination," *J. Hazardous Mater.*, 143, 118 (2007).
- [52] Chatterjee, D. and A. Mahata, "Photoassisted Detoxification of Organic Pollutants on the Surface Modified TiO₂ Semiconductor Particulate System," *Catal. Commun.*, 2, 1 (2001).
- [53] Cherian, S. and C. C. Wamser, "Adsorption and Photoactivity of Tetra(4-carboxyphenyl) Porphyrin (TCPP) on Nanoparticulate TiO₂," *J. Phys. Chem. B*, 104, 3624 (2000).
- [54] Cho, Y., W. Choi, C. H. Lee, T. Hyeon and H. I. Lee, "Visible Light-induced Degradation of Carbon Tetrachloride on Dye-sensitized TiO₂," *Environ. Sci. Technol.*, 35, 966 (2001).
- [55] Cho, Y. and W. Choi, "Visible Light-induced Reactions of Humic Acids on TiO₂," *J. Photochem. Photobiol. A: Chem.*, 148, 129 (2002).
- [56] d'Henezela, O., P. Pichat, and D. F. Ollis, "Benzene and Toluene Gas-phase Photocatalytic Degradation over H₂O and HCl Pretreated TiO₂: By-products and Mechanisms," *J. Photochem. Photobiol. A: Chem.*, 118, 197 (1998).
- [57] De Rivas, B., J. I. Gutierrez-Ortiz, R. Lopez-Fonseca, and J. R. Gonzalez-Velasco, "Analysis of the Simultaneous Catalytic Combustion of Chlorinated Aliphatic Pollutants and Toluene over Ceria-zirconia Mixed Oxides," *Appl. Catal. A: General*, 314, 54 (2006).
- [58] Domingueza, C., J. Garcia, M. A. Pedraz, A. Torres, and M. A. Galan, "Photocatalytic Oxidation of Organic Pollutants in Water," *Catal. Today*, 40, 85 (1998).
- [59] Einag, H., S. Futamura, and T. Ibusuki, "Heterogeneous Photocatalytic Oxidation of Benzene, Toluene, Cyclohexene and Cyclohexane in Humidified Air: Comparison of Decomposition Behavior on Photoirradiated TiO₂ Catalyst," *Appl. Catal. B: Environ.*, 38, 215 (2002).
- [60] Fujii, Y., Y. Tsukahara, and Y. Wada, "pH-dependent Reversible Switching of Fluorescence of Water-soluble Porphyrin Adsorbed on Mesoporous TiO₂ Film," *Bull. Chem. Soc. Jpn.*, 79, 561 (2006).
- [61] Fujishima, A., T. N. Rao, and D. A. Tryk, "Titanium Dioxide Photocatalysis," *J. Photochem. Photobiol. C: Photochem. Rev.*, 1, 1 (2000).
- [62] Gratzel, M., "Photoelectrochemical Cells," *Nature*, 414, 338 (2001) [63] Hagfeldt, A. and M. Gratzel, "Molecular Photovoltaics," *Acc.*

- Chem. Res., 33, 269 (2000) [64]Houling, V.H. and M. Gratzel, "Photochemical H₂ Generation by Visible Light. Sensitization of TiO₂ Particles by Surface Complexation with 8-Hydroxyquinoline," J. Am. Chem. Soc., 105, 5695 (1983).
- [65]Huijsers, A., T. Savenije, A. Kotlewski, S. Picken, and L. Siebbeles, "Efficient Light-harvesting Layers of Homeotropically Aligned Porphyrin Derivatives," Adv. Mater., 18, 2234 (2006).
- [66]Hoffmann, M., S. Martin, W. Choi, and D. Bahnemann, "Environmental Applications of Semiconductor Photocatalysis," Chem. Rev., 95, 69 (1995).
- [67]Iliev, V. and D. Tomova, "Photocatalytic Oxidation of Sulfide ion Catalyzed by Phthalocyanine Modified Titania," Catal. Commun., 3, 287 (2002).
- [68]Iliev, V., "Phthalocyanine-modified Titania - Catalyst for Photooxidation of Phenols by Irradiation with Visible Light," J. Photochem. Photobiol. A: Chem., 151, 195 (2002).
- [69]Jeong, J., K. Sekiguchi, and K. Sakamoto, "Photochemical and Photocatalytic Degradation of Gaseous Toluene Using Short-wavelength UV Irradiation with TiO₂ Catalyst: Comparison of Three UV Sources," Chemosphere, 57, 663 (2004).
- [70]Jin, Z., X. Zhang, Y. Li, S. Li, and G. Lu, "5.1% Apparent Quantum Efficiency for Stable Hydrogen Generation over Eosin-sensitized CuO/TiO₂ Photocatalyst under Visible Light Irradiation," Catal. Commun., 8, 1267 (2007).
- [71]Kalyanasundaram, K. and M. Gratzel, "Applications of Functionalized Transition Metal Complexes in Photonic and Optoelectronic Devices," Coord. Chem. Rev., 77, 347 (1998).
- [72]Keller, N., E. Barraud, F. Bosc, D. Edwards, and V. Keller, "On the Modification of Photocatalysts for Improving Visible Light and UV Degradation of Gas-phase Toluene over TiO₂," Appl. Catal. B: Environ., 70, 423 (2007).
- [73]Kim, S.B. and S. C. Hong, "Kinetic Study for Photocatalytic Degradation of Volatile Organic Compounds in Air Using Thin Film TiO₂ Photocatalyst," Appl. Catal. B: Environ., 35, 305 (2002).
- [74]Lewandowski, M. and D. F. Ollis, "Halide Acid Pretreatments of Photocatalysts for Oxidation of Aromatic Air Contaminants: Rate Enhancement, Rate Inhibition, and a Thermodynamic Rationale," J. Catal., 217, 38 (2003).
- [75]Linsebigler, A., G. Lu, and J. Yates, "Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results," Chem. Rev., 95, 735 (1995).
- [76]Maira, A.J., K. L. Yeung, J. Soria, J. M. Coronado, C. Belver, C. Y. Lee, and V. Augugliaro, "Gas-phase Photo-oxidation of Toluene Using Nanometer-size TiO₂ Catalysts," Appl. Catal. B: Environ., 29, 327 (2001).
- [77]Marci, G., M. Addamo, V. Augugliaro, S. Coluccia, E. Garcia-Lopez, V. Loddo, G. Martra, L. Palmisano, and M. Schiavello, "Photocatalytic Oxidation of Toluene on Irradiated TiO₂: Comparison of Degradation Performance in Humidified Air Water and in Water Containing a Zwitterionic Surfactant," J. Photochem. Photobiol. A: Chem., 160, 105 (2003).
- [78]Mo, J., Y. Zhang, Q. Xu, and R. Yang, "Effect of TiO₂ /Adsorbent Hybrid Photocatalysts for Toluene Decomposition in Gas Phase," J. of Hazardous Mater., 168, 276 (2009).
- [79]Moon, J., C. Y. Yun, K. W. Chung, M. S. Kang, and J. Yi, "Photocatalytic Activation of TiO₂ under Visible Light Using Acid Red 44," Catal. Today, 87, 77 (2003).
- [80]Nakajima, A., H. Obata, Y. Kameshima, and K. Okada, "Photocatalytic Destruction of Gaseous Toluene by Sulfated TiO₂ Powder," Catal. Commun., 6, 716 (2005).
- [81]Nasr, C., K. Vinodgopal, L. Fisher, S. Hotchandani, A. K. Chattopadhyay, and P. Kamat, "Environmental Photochemistry on Semiconductor Surfaces. Visible Light Induced Degradation of a Textile Diazo Dye, Naphthol Blue Black, on TiO₂ Nanoparticles," J. Phys. Chem., 100, 8436 (1996).
- [82]Obee, T. and R. Brown, "TiO₂ Photocatalysis for Indoor Air Applications: Effects of Humidity and Trace Contaminant Levels on the Oxidation Rates of Formaldehyde, Toluene, and 1% Butadiene," Environ. Sci. Technol., 29, 1223 (1995).
- [83]Obee, T., "Photooxidation of Sub-Parts-Per-Million Toluene and Formaldehyde Levels on Titania Using a Glass-Plate Reactor," Environ. Sci. Technol., 30, 3578 (1996).
- [84]Odobel, F., E. Blart, M. Lagre ' e, M. Villieras, H. Boujtita, N. Murr, S. Caramoric, and C. A. Bignozzi, "Porphyrin Dyes for TiO₂ Sensitization," J. Mater. Chem., 13, 502 (2003) [85]Ozcan, O., F. Yukruk, E. U. Akkaya, and D. Uner, "Dye Sensitized Artificial Photosynthesis in the Gas Phase over Thin and Thick TiO₂ Films under UV and Visible Light Irradiation," Appl. Catal. B: Environ., 71, 291 (2007).
- [86]Robertson, N., "Optimizing Dyes for Dye-sensitized Solar Cells," Angew. Chem. Int. Ed., 45, 2338 (2006).
- [87]Ross, H., J. Bendig, and S. Hecht, "Sensitized Photocatalytical Oxidation of Terbutylazine," Solar Energy Mater. Solar Cells, 33, 475 (1994).
- [88]M. Voinov and J. Augustynski in Schiravello, M.(Editor), Heterogeneous Photocatalysis, p.8, John-Wiley and Sons, Inc., New York, U.S.A. (1997) [89]Sekiguchi, K., A. Sanada, and K. Sakamoto, "Degradation of Toluene with an Ozone-Decomposition Catalyst in the Presence of Ozone, and the Combined Effect of TiO₂ Addition," Catal. Commun., 4, 247 (2003).
- [90]Sekiguchi, K., K. Yamamoto, and K. Sakamoto, "Photocatalytic Degradation of Gaseous Toluene in an Ultrasonic Mist Containing TiO₂ Particles," Catal. Commun., 9, 281 (2008).

- [91]Shiraishi, F. and T. Ishimatsu, " Toluene Removal from Indoor Air Using a Miniaturized Photocatalytic Air Purifier Including a Preceding Adsorption/Desorption Unit, " Chem. Eng. Sci., 64, 2466 (2009).
- [92]Smestad, G.P., " Education and Solar Conversion: Demonstrating Electron Transfer, " Solar Energy Mater. Solar Cells, 55, 157 (1998).
- [93]Strini, A., S. Cassese, and L. Schiavi, " Measurement of Benzene, Toluene, Ethylbenzene and o-Xylene Gas Phase Photodegradation by Titanium Dioxide Dispersed in Cementitious Materials Using a Mixed Flow Reactor, " Appl. Catal. B: Environ., 61, 90 (2005).
- [94]Subrahmanyam, Ch., A. Renken, and L. Kiwi-Minsker, " Catalytic Abatement of Volatile Organic Compounds Assisted by Non-Thermal Plasma, Part II. Optimized Catalytic Electrode and Operating Conditions, " Appl. Catal. B: Environ., 65, 157 (2006).
- [95]Vinodgopal, K. and D. Wynkoop, " Environmental Photochemistry on Semiconductor Surfaces: Photosensitized Degradation of a Textile Azo Dye, Acid Orange 7, on TiO₂ Particles Using Visible Light, " Environ. Sci. Technol., 30, 1660 (1996).
- [96]Wang R. C., K. S. Fan, and J. S. Chang, " Removal of Acid Dye by ZnFe₂O₄/TiO₂-immobilized Granular Activated Carbon under Visible Light Irradiation in a Recycle Liquid – Solid Fluidized Bed, " J. Taiwan Inst. Chem. Eng., 40, 533(2009)
- [97]Watson, D.F. and G. J. Meyer, " Electron Injection at Dye-sensitized Semiconductor Electrodes, " Annu. Rev. Phys. Chem., 56, 119 (2005).
- [98]Yen, W. T., Y. C. Lin, P. C. Yao, J.H. Ke, and Y.L. Chen, " Growth Characteristics and Properties of ZnO:Ga Thin Films Prepared by Pulsed DC Magnetron Sputtering, " Appl. Surf. Sci., 256, 3432 (2010).
- [99]Yu, J. and X. Zhao, " Effect of Surface Treatment on the Photocatalytic Activity and Hydrophilic Property of the Sol-Gel Derived TiO₂ Thin Films, " Mater. Res. Bull., 36, 97 (2001).
- [100]Yu, J.C, J. Yu, and J. Zhao, " Enhanced Photocatalytic Activity of Mesoporous and Ordinary TiO₂ Thin Films by Sulfuric Acid Treatment, " Appl. Catal. B: Environ., 36, 31 (2002).
- [101]Zhang, P. F. Liang, G. Yu, Q. Chen, and W. Zhu, " A Comparative Study on Decomposition of Gaseous Toluene, " J. Photochem. Photobiol. A: Chem., 156, 189 (2003).
- [102]Zhang, Y., J. C. Crittenden, D. W. Hand, and D. L. Perram, " Fixed-bed Photocatalysts for Solar Decontamination of Water, " Environ. Sci. Technol., 28, 435 (1994).
- [103] H. L. Hartnagel, A. K. Jain and C. Tagadish, " Semiconducting Transparent Thin Films " ,published by Institute of Physics Publication, 1995, P. 17.
- [104]K. Ellmer, A. Klein, B. Rech, " Transparent Conductive Zinc Oxide: Basics and Applications in Thin Film Solar Cells " , Springer, illustrated edition (2007)
- [105] P. Nunes, E. Fortunato, P. Tonello, F.B. Fernandes, P. Vilarinho, R. Martins, Vacuum 64 (2002) 281.
- [106] R.J. Hong, X. Jiang, B. Szyzka, V. Sittinger, A. Pflug, Appl. Surf. Sci. 207 (2003) 341.
- [107] M. de la L. Olvera, A. Maldonado, R. Asomoza, Sol. Energy Mater. Sol. Cells 73 (2002) 425.
- [108] C.H. Lee, L.Y. Lin, Appl. Surf. Sci. 92 (1996) 163.
- [109] Y. Natsume, H. Sakata, Mater. Chem. Phys. 78 (2002) 170.
- [110] C.H. Lee, K.S. Lim, Jinsoo Song, Jpn. J. Appl. Phys. 36 (1997) 4418.
- [111] H. Mondragon Suarez, A. Maldonado, M. de la L. Olvera, A. Reyes, R. Castanedo Perez, G. Torres Delgado, R. Asomoza, Appl. Surf. Sci. 193 (2002) 52.
- [112] A. Suzuki, T. Matsushita, N. Wada, Y. Sakamoto, M. Okuda, Jpn. J. Appl. Phys. 35 (1996) L56.
- [113] J.-H. Lee, B.-O. Park, Thin Solid Films 426 (2003) 94.
- [114] J. D. Mackenzie, in " Ultrastructure Processing of Ceramics, Glass and Composites " , eds. L. L. Hench and D. R. Ulrich, p15 wiley , New York, 1984.
- [115]謝曙旭, " 以溶凝膠法在低溫下製備奈米級PTO及PZT粉末及其相變化與低溫燒結之研究 " , 國立清華大學材料科學與工程研究所, 民國93年6月.
- [116] Calzada, M. L.; Sirela, R.; Carmona, F.; Jimenez, B. Investigations of a diol based sol-gel process for the preparation of lead titanate materials. J. Am. Ceram. Soc. 1995, 77, 1802-1808.
- [117]Ulrich, S.; Nicola, H.; Lorenz, A. Hybrid inorganic-organic materials by sol-gel processing of organofunctional metal alkoxides. Chem. Mater. 1995, 7, 2010-2017.
- [118] R. R. Bhave, Inorganic membranes synthesis, characteristics and applications, Van Nostrand Reinhold, 1991.
- [119] 謝坤龍, " 鈹銀合金/氧化鋁複合膜之特性研究:以溶凝膠法修飾基材孔徑之探討 " , 國立成功大學化學工程研究所碩士論文 (2000)
- [120] R. J. Gonzalez, R. Zallen, and H. Beger, Phys. Rev. B, 55, 7014 (1997).
- [121] J. S. Kasper and K. D. Lomdsale, " International tables of X-ray crystallography " , 2nd edition (1959).
- [122] T. E. Weirich, M. Winterer, S. Seifried, H. Hahn, and H. Fuess, Ultramicroscopy, 81, 263, (2000).
- [123] Powder Diffraction File, Card No. 21-1272, Joint committee on powder diffraction standards, Swarthmore, PA.
- [124] Powder Diffraction File, Card No. 21-1276, Joint committee on powder diffraction standards, Swarthmore, PA.
- [125] J. Muscat, N. M. Harrison, and G. Thornton, Phys. Rev. B, 59, 2320 (1999).
- [126]A. Fujishima, K. Hashimoto, and T. Watanabe, " TiO₂ Photocatalysis Fundamentals and Applications " , 1st edition, BKC Inc. (1999).
- [127] R. Benedix, F. Dehn, J. Quaas, and M. Orgass, LACER, 5, 157 (2000).

- [128] A. Fujishima, K. Hashimoto, and T. Watanabe, "TiO₂ Photocatalysis Fundamentals and Applications", 1st edition, BKC Inc. (1999).
- [129] Gratzel, M., 2001. Photoelectrochemical cells. *Nature* 414, 338 – 344.
- [130] Lee, S.Y., Park, J., Joo, H., 2006. Visible light-sensitized photocatalyst immobilized on beads by CVD in a fluidizing bed. *Solar Energy Material & Solar Cells* 90, 1905 – 1914.
- [131] Srinivasan, S.S., Wade, J., Stefanakos, E.K., 2005. Visible light photocatalysis via nano-composite CdS-TiO₂ materials. *Material Research Society Symposium Proceeding* 876E, R5.2.1 – R5.2.8.
- [132] Cheng, P., Li, W., Zhou, T., Jin, Y., Gu, M., 2004. Physical and photocatalytic properties of zinc ferrite doped titania under visible light irradiation. *Journal of Photochemistry and Photobiology A: Chemistry* 168, 97 – 101.
- [133] Ding, H., Sun, H., Shan, Y., 2005. Preparation and characterization of mesoporous SBA-15 supported dye-sensitized TiO₂ photocatalyst. *Journal of Photochemistry and Photobiology A: Chemistry* 169, 101 – 107.
- [134] Kamat, P.V., Fox, M.A., 1983. Photosensitization of TiO₂ colloids Erythrosine B in acetonitrile. *Chemical Physics Letters* 102(4), 379 – 384.
- [135] Patrick, B., Kamat, P.V., 1992. Photoelectrochemistry in semiconductor particulate systems. 17. Photosensitization of large-bandgap semiconductor: charge injection from triplet excited thionine into zinc oxide colloids. *The Journal of Physical Chemistry* 96(3), 1423 – 1428.
- [136] Vlachopoulos, N., Liska, P., Augustynski, J., Gratzel, M., 1988. Very efficient visible light energy harvesting and conversion by spectral sensitization of high surface area polycrystalline titanium dioxide films. *Journal of the American Chemical Society* 110(4), 1216 – 1220.