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Titanium Dioxide Sol-gel Schottky Diodes and Effect of Titanium Dioxide Nanoparticle

Mohammad Maniruzzaman*, Lindong Zhai* Seongcheol Mun* and Jaehwan Kim†

Abstract – This paper reports the effect of Titanium dioxide (TiO_2) nanoparticles on a TiO_2 sol-gel Schottky diode. TiO_2 nanoparticles were blended with TiO_2 sol-gel to fabricate the Schottky diode. TiO_2 nanoparticles showed strong anatase and rutile X-ray diffraction peaks. However, the mixture of TiO_2 sol-gel and TiO_2 nanoparticles exhibited no anatase and rutile peaks. The forward current of the Schottky diode drastically increased as the concentration of TiO_2 nanoparticles increased up to 10 wt. % and decreased after that. The possible conduction mechanism is more likely space charge limited conduction.

Keywords: Schottky diode, Nanoparticle, Titanium dioxide, Sol-gel

1. Introduction

Recently metal oxides have attracted great attention due to their remarkable optical, physical, chemical, and electronic properties [1, 2]. Among the metal oxides, titanium oxide (TiO_2) has a wide range of advantageous properties, such as chemical stability, photocatalytic activity, photosensitivity, and electrical conductivity and is applicable to electronic devices, chemical sensors, photocatalysts, solar cells, and photoelectrochemical cells [3-6]. These properties strongly depend on crystallite size and shape of the TiO_2. TiO_2 has three main crystalline structures including anatase, rutile and brookite. Each structure has unique chemical, physical, and electronic properties and leads different applications.

TiO_2 thin films have been fabricated with a variety of techniques including sol-gel process, sputtering with different metallic and ceramic targets, ion beam enhanced deposition, chemical vapor deposition, and pulsed laser deposition. Sol-gel process is one of the most important techniques to synthesize various functional materials. It has advantages over conventional other techniques in terms of low temperature process, large area coating, homogeneous and multi-component metal oxide preparation and low equipment cost. Although sol-gel process has such a superior advantages, the final material performance is greatly affected by the process conditions including species of solvent, concentration of TiO_2 and heating process.

In this paper, we report the fabrication of a Schottky diode made by mixing TiO_2 nanoparticles and TiO_2 sol-gel. Schottky diodes have been made with inorganic semiconducting material, conducting polymers and a combination of both materials [7-10]. The effect of TiO_2 nanoparticles in the TiO_2 sol-gel for the performance of Schottky diode is investigated in terms of surface field emission scanning electron microscope (FESEM) images, x-ray diffraction (XRD) patterns and current-voltage (I-V) characteristics of the fabricated Schottky diode. Three possible conduction mechanisms are explained to determine dominant conduction process in the device.

2. Experimental procedure

TiO_2 nanoparticles (~30 nm) were purchased from Aldrich Co. and used without further purification. The TiO_2 sol was fabricated by titanium (IV) isopropoxide (TIP, 97 %), ethanol (99.8 %), HCl (36.4 %) and deionized (DI) water. The sol was prepared as follows: 50 ml of ethanol was charged in the 100 ml of round bottom flask, and 6 g of TIP was added to the solution. Then, HCl was added to the mixture until the solution became transparent with stirring, and the solution was kept under vigorous stirring for 1 day. The aqueous TiO_2 nanoparticle solution was directly mixed with TiO_2 sol-solution with 1 wt% (TiO-1), 5 wt% (TiO-5), 10 wt% (TiO-10), and 15 wt% (TiO-15) TiO_2 nanoparticle concentrations. The various concentrations of TiO_2 nanoparticles and TiO_2 sol mixtures were spin coated on a silicon wafer with 2000 rpm. The film was then heated at 300°C for 1 h in a tube furnace under nitrogen gas purging. The silicon wafer was cleaned by a mixture of sulfuric acid and hydrogen peroxide in an ultrasonic cleaner, followed by cleaning and rinsing with de-ionized water. Finally, the wafer was washed with acetone and dried at 100°C for 30 minutes. The film thickness was approximately 100nm after heat treatment. Al electrode was then vacuum-deposited onto the film. Fig. 1 shows the three-layered Schottky diode structure.

† Corresponding Author: Dept. of Mech. Eng., Inha University, Korea. (jaehwan@inha.ac.kr)
* Dept. of Mech. Eng., Inha University, Korea. (mamun08me@yahoo.com, duicaofei@naver.com, bobtf@daum.net)
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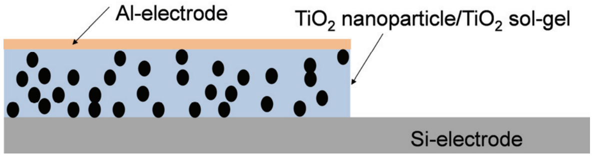


Fig. 1. Three-layered Schottky diode structure: TiO_2 nanoparticle-TiO_2 sol-gel acts as a semiconducting layer.

The silicon layer was used as an electrode.

3. Results and Discussion

Fig. 2 shows surface FESEM images of (a) TiO-1, (b) TiO-5, (c) TiO-10, and (d) TiO-15. Nanoparticles were not observed on the surface of the TiO-1 film. Small individual particles were observed for the TiO-5. As the concentration of TiO_2 nanoparticles increased more than 10%, aggregated particles were observed on the surface of the films as shown in Fig. 2 (d). Fig. 2(e) shows the cross sectional FESEM image of TiO-10. The thickness of the TiO_2 layer is about 75 nm.

Anatase and rutile crystallite phases are the main structures of TiO_2, which have band-gap energies of 3.2 and 3.0 eV, respectively [11, 12]. Anatase TiO_2 has excellent photocatalytic activity, long-term stability and nontoxicity [13]. Sol-gel spin-coating process is a promising technique over the other conventional techniques. The prepared films are mostly amorphous phase structures [14]. Fig. 3(a) shows the XRD patterns for the TiO-1, TiO-5, TiO-10 and TiO-15. There is no clear anatase or rutile diffraction peak for the TiO-1 and TiO-5. However, very weak major anatase (101) and rutile (110) diffraction peaks were observed for the TiO-10 and TiO-15. Fig. 3(b) shows XRD pattern for the TiO_2 nanoparticles. Strong anatase (101) and rutile (110) peaks are located at 25.4° and 27.5° respectively. The relative intensities of the anatase and rutile diffraction peaks are 54.7 and 45.3 %, respectively. It is clear that the TiO_2 nanoparticles are composed of anatase and rutile crystal structures.

Schottky diodes fabricated with mixture of TiO_2 sol-gel and TiO_2 nanoparticles with different concentrations were characterized by measuring their I-V characteristics. The work function of Al is low (approximately 4.1 eV) compared with TiO_2 (5.1 eV for anatase structure and 4.9 eV for rutile structure) [11]. Therefore, the Al and TiO_2 nanoparticles and TiO_2 sol contact might be a Schottky junction due to a big difference in the work functions. Furthermore, due to the similar work function of Si (4.52 eV) and TiO_2, the Si and TiO_2 nanoparticles and TiO_2 sol junction could be an Ohmic contact. Fig. 4 shows the result. The forward bias current was approximately 30 μA for the Schottky diode fabricated with pure TiO_2 sol-gel without TiO_2 nanoparticles. The forward current for the TiO-1 is approximately 130 μA, which is 4 times higher than the pure sol-gel Schottky diode. As the amount of TiO_2

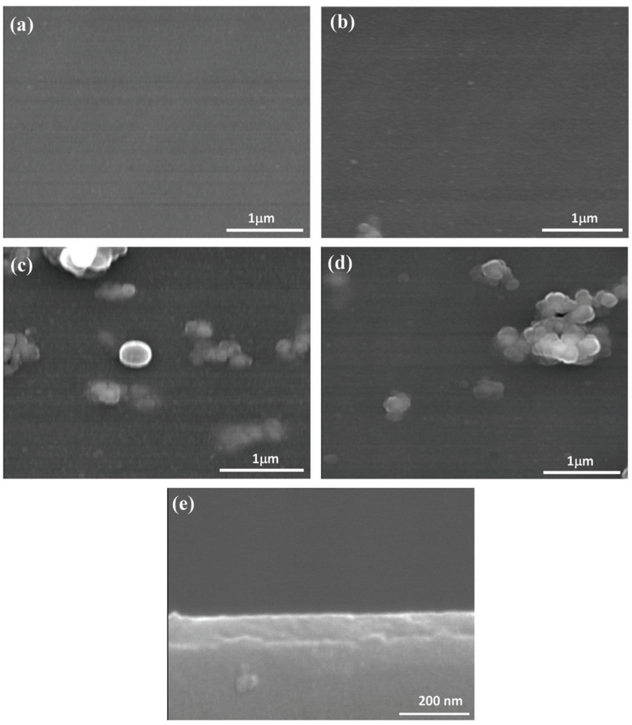


Fig. 2. FESEM surface images: (a) TiO-1; (b) TiO-5; (c) TiO-10; (d) TiO-15 and (e) FESEM cross-sectional image of TiO-10.

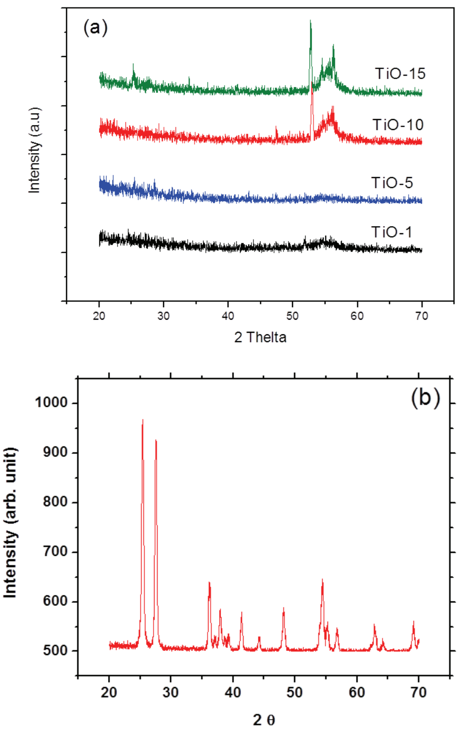


Fig. 3. XRD patterns: (a) TiO-1; TiO-5, TiO-10, and TiO-15. (b) TiO_2 nanoparticles.

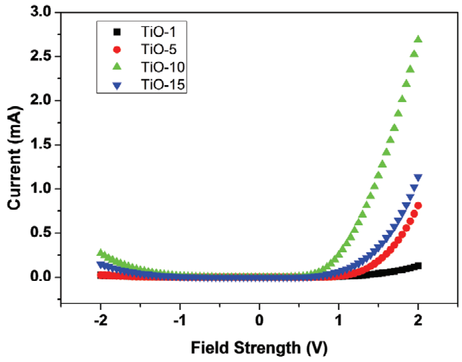
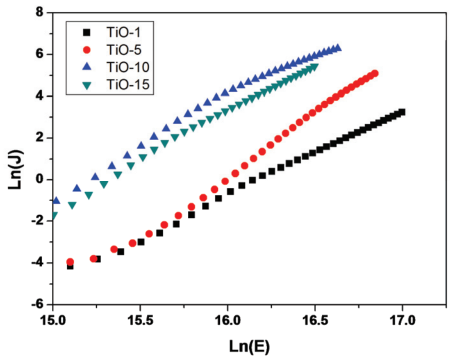
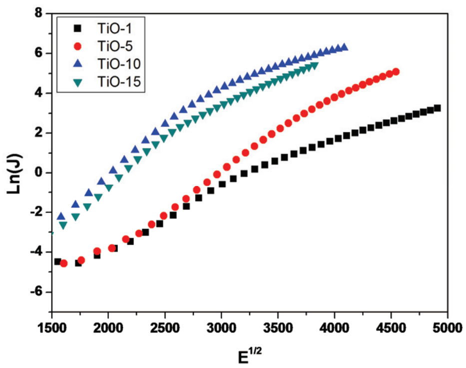


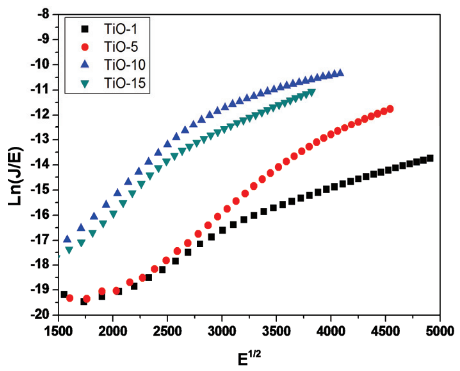
Fig. 4. I-V characteristics of Schottky diodes.



(a)



(b)



(c)

Fig. 5. The plots of three conduction mechanisms: (a) Ln (J) vs Ln(V) for SCLC. (b) Ln(J) vs $E^{1/2}$ for SC and (c) Ln(J/V) vs $E^{1/2}$ for PFC.

Table 1. Beta values of TiO_2 nanoparticle doped TiO_2 sol-gel Schottky diodes of Schottky emission and Poole-Frenkel emission. Unit: $\times 10^{-5}$ eV/ (V/m)$^{1/2}$

Samples	Schottky emission	Poole-Frenkel emission
TiO-1	13.951	4.392
TiO-5	18.085	6.975
TiO-10	19.119	12.659
TiO-15	19.345	6.459

nanoparticles increased, the forward current drastically increased up to 10 wt. % and decreased thereafter. The maximum forward current of 2.7 mA was achieved at 10 wt. % of TiO_2 nanoparticles. The improved forward current is due to the high quality crystallite nanoparticles of TiO_2, which drastically increase the surface area of the active material. The reduction of the forward current for the TiO-15 might be due to the aggregation of the TiO_2 nanoparticles as shown in Fig. 2 (d).

To distinguish the major conduction mechanism, various plots were employed based on the theoretical equation of each conduction mechanism. Three conduction models were employed by plotting Ln(J) versus Ln(V), Ln(J) versus $E^{1/2}$ and Ln(J/V) versus $E^{1/2}$ for the space charge limited conduction (SCLC), Schottky conduction (SC) and Poole-Frenkel conduction (PFC) models, respectively. Fig. 5 (a), (b) and (c) represent the plots based on the SCLC, SC and PFC models, respectively. Table 1 shows beta values of SC and PFC mechanisms in linear regime. For both cases, beta values are too big compared with the theoretical values (3.03×10^{-5} eV/ (V/m)$^{1/2}$ for SC and 6.06×10^{-5} eV/(V/m)$^{1/2}$ for PFC) to match these mechanisms at low electric field [15]. The plot of SCLC model shown in Fig. 5(c) shows best linear fit in the experimental range. Therefore, SCLC process could be a major conduction mechanism [16].

4. Conclusion

The mixtures of TiO_2 sol-gel and TiO_2 nanoparticles with different concentrations of TiO_2 nanoparticles were used as a semiconducting material for a Schottky diode fabrication. Although TiO_2 nanoparticles show strong anatase and rutile XRD peaks, the mixtures of TiO_2 sol-gel and TiO_2 nanoparticles exhibit no characteristic anatase and rutile diffraction peak. The forward current drastically increased as the concentration of TiO_2 nanoparticles increased until 10 wt. %. The forward current decreased as the TiO_2 concentration further increased. SCLC mechanism might be dominant for the linear regime.

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References

[1] T.L. Chen, Y. Furubayashi, Y. Hirose, T. Hitosugi, T. Shimada and T. Hasegawa, "Anatase phase stability and doping concentration dependent refractivity in codoped transparent conducting TiO_2 films," *J. Phys. D: Appl. Phys.*, vol. 40, no. 19, pp. 5961-5964, Oct. 2007.

[2] O.V. Sakhno, L.M. Goldenberg, J. Stumpe and T.N. Smimova, "Surface modified ZrO_2 and TiO_2 nanoparticles embedded in organic photopolymers for highly effective and UV-stable volume holograms," *Nanotechnol.,* vol.18, no.10, pp.105704, Mar. 2007.

[3] E.W. McFarland and J. Tang, "A photovoltaic device structure based on internal electron emission," *Nature,* vol. 421, pp. 616-618, Feb. 2003.

[4] H. Miyazaki, T. Hyodo, Y. Shimizu and M. Egashira, "Hydrogen-sensing properties of anodically oxidized TiO_2 film sensors: Effects of preparation and pretreatment conditions," *Sensor Actuat. B-Chem.,* vol. 108, pp. 467-472, July 2005.

[5] P. Yu, K. Zhu, A.G. Norman, S. Ferrere, A.J. Frank and A.J. Nozik, "Nanocrystalline TiO_2 Solar Cells Sensitized with InAs Quantum Dots," *J. Phys. Chem. B,* vol. 110, no. 50, pp. 25451-25454, Nov. 2006.

[6] G. Wang, H. Chen, H. Zhang, Y. Shen, C. Yuan, Z. Lu, G. Wang and W. Yang, "Current-voltage characteristics of TiO_2 /PPy complex films," *Phys. Lett. A,* vol. 237, no. 3, pp. 165-168, Jan. 1998.

[7] C. Chen, W. Zhang, B. Zhao and Y. Zhang, "Investigation of Schottky-Barrier carbon nanotube field-effect transistor by an efficient semi-classical numerical modeling," *Phys. Lett. A*, vol. 374, no. 2, pp. 309-312, Dec. 2009.

[8] S.Y. Yang, J. Kim and K.D. Song, "Flexible patch rectennas for wireless actuation of cellulose electro-active paper actuator," *JEET*, vol.7, no.6, pp.954-958, Nov. 2012.

[9] J. Nayak, S.K. Mahadeva, Y. Chen, K.S. Kang and J. Kim, "Effect of ionic liquid dispersion on performance of a conducting polymer based Schottky diode," *Thin Solid Films,* vol. 518, no. 19, pp. 5626-5628, July 2010.

[10] K.S. Kang, K.J. Han and J. Kim, "Polymer-Based Flexible Schottky Diode Made With Pentacene–PEDOT: PSS," *Nanotechnol., IEEE Trans.*, vol. 8, no. 5, pp.627-630, Sep. 2009.

[11] A. Sclafani, L. Palmisano and M. Schiavello, "Influence of the preparation methods of titanium dioxide on the photocatalytic degradation of phenol in aqueous dispersion," *J. Phys. Chem.,* vol.94, no.2, pp. 829-832, Jan. 1990.

[12] M.V. Rao, K. Rajeshwar, V.R. Pai Verneker and J. Dubow, "Photosynthetic production of hydrogen and hydrogen peroxide on semiconducting oxide grains in aqueous solutions," *J. Phys. Chem.,* vol.84, no.15, pp. 1987-1991, July 1980.

[13] Z. Zhao and Q. Liu, "Mechanism of higher photocatalytic activity of anatase TiO_2 doped with nitrogen under visible-light irradiation from density functional theory calculation," *J. Phys. D: Appl. Phys.,* vol.41, no.2, pp.025105, Jan. 2008.

[14] H. Rath, P. Dash, T. Som, P.V. Satyam, U.P. Singh, P.K. Kulriya, D. Kanjilal, D.K. Avasthi and N.C. Mishra, "Structural evolution of TiO_2 nanocrystalline thin films by thermal annealing and swift heavy ion irradiation," *J. Appl. Phys.*, vol.105, no.7, pp.074311, Apr. 2009.

[15] K.H. Yoo, K.S. Kang, Y. Chen, K.J. Han, J. Kim, "Direct and indirect contact effect between Al and TiO_2 on the conduction mechanism for polymer-TiO_2 Schottky diodes," *J. Phys. D: Appl. Phys*., vol.42, no. 7, pp. 075107, Feb. 2009.

[16] K.H. Yoo, K.S. Kang, Y. Chen, K.J. Han and J. Kim, "The effect of TiO_2 nanoparticle concentration on conduction mechanism for TiO_2-polymer diode," *Appl. Phys. Lett.,* vol.93, no.19, pp.192113, Nov. 2008.

Mohammad Maniruzzaman He received B.S degree in Industrial & Production Engineering in 2009 from Bangladesh University of Engineering and Technology, MS in Mechanical Engineering from Inha University 2011. And now he is PhD student in Institute for Frontier Materials in Deakin University. His research interests are cellulose, nanocomposite, biosensors, liquid plasma, plant biology and plasma medicine.

Lindong Zhai He received his B.E. in Automotive and Mechanical Engineering in 2011 from Howon University and M.S. in Mechanical Engineering in 2013 from Inha University. Now he is PhD student in Mechanical Engineering in Inha University. His research is focus on cellulose nanocrystal and nanofiber.

Seongcheol Mun He received his B.S. and M.S. degrees of Mechanical Engineering from Inha University in 2010 and 1012, respectively. He is now Ph.D. student in Mechanical Engineering, Inha University. His research interests are renewable smart materials and its device applications.

Jaehwan Kim Prof. Kim received his Ph.D. degree of Engineering Science and Mechanics from The Pennsylvania State University, USA, in 1995. Since then he joined Mechanical Engineering department of Inha University where he is now Inha Fellow Professor. Prof. Kim is a fellow of The National Academy of Engineering of Korea and The Korean Academy of Science and Technology. His research interests are smart materials such as piezoelectric materials, electro-active polymers, electro-active paper, and smart devices such as sensors, actuators, motors and MEMS.