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 crystal lattice 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 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.

Fig. 1 shows the three-layered Schottky diode structure.
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 TiO2 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 TiO2 layer is about 75 nm.

Anatase and rutile crystallite phases are the main structures of TiO2, which have band-gap energies of 3.2 and 3.0 eV, respectively [11, 12]. Anatase TiO2 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 TiO2 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 TiO2 nanoparticles are composed of anatase and rutile crystal structures.

Schottky diodes fabricated with mixture of TiO2 sol-gel and TiO2 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 TiO2 (5.1 eV for anatase structure and 4.9 eV for rutile structure) [11]. Therefore, the Al and TiO2 nanoparticles and TiO2 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 TiO2, the Si and TiO2 nanoparticles and TiO2 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 TiO2 sol-gel without TiO2 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 TiO2...
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$/ (V/m)^{1/2}$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Schottky emission</th>
<th>Poole-Frenkel emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO-1</td>
<td>13.951</td>
<td>4.392</td>
</tr>
<tr>
<td>TiO-5</td>
<td>18.085</td>
<td>6.975</td>
</tr>
<tr>
<td>TiO-10</td>
<td>19.119</td>
<td>12.659</td>
</tr>
<tr>
<td>TiO-15</td>
<td>19.345</td>
<td>6.459</td>
</tr>
</tbody>
</table>

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 ($3.03 \times 10^{-5}$ eV$/ (V/m)^{1/2}$ for SC and $6.06 \times 10^{-5}$ 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.

Acknowledgements

This work was performed under the support of National Research Foundation of Korea (NRF-2013M3C1A3059586).
References


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 2012, 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.