การประดิษฐ์และสมบัติที่เกิดจากรอยสัมผัสช๊อททก์กี้ระหว่างทองคำและท่อนาโนไททาเนีย

The Fabrication and Properties of Schottky Contact between Au/TiO_2 Nanotubes Semiconductors

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บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาเกี่ยวกับสมบัติที่เกิดจากรอยสัมผัสช๊อททก์กี้ระหว่างโลหะทองคำและท่อนาโนไททาเนีย โครงสร้างจุลภาคและลักษณะพื้นผิวของท่อนาโนไททาเนียได้ถูกศึกษาโดยวิธีการ XRD SEM และ XPS ชั้นบางๆ ของทองคำที่มีความหนาในระดับไมครอนได้ถูกเคลือบบนผิวของท่อนาโนไททาเนีย โดยวิธีการไอระเหยด้วยความร้อน หัววัดแบบสองขั้วถูกใช้วัดเพื่อยืนยันรอยสัมผัสช๊อททก์กี้ เส้นกราฟความสัมพันธ์ลักษณะของกระแสและความต่างศักย์ไฟฟ้าสามารถถูกอธิบายสมบัติที่เกิดขึ้นโดยใช้แผนภาพทางโครงสร้างพลังงาน

คำสำคัญ: รอยสัมผัสช๊อททก์กี้ ความหนาของทองในระดับไมโคร ท่อนาโนไททาเนีย

Abstract

This work aims to investigate the phenomena of Schottky barrier between Au/TiO_2 nanotubes. The microstructure and surface morphologies of TiO_2 nanotubes were characterized by XRD, SEM and XPS. Micro-layers of Au were deposited on TiO_2 nanotubes surface by thermal evaporation. The two electronic probes were employed to confirm Schottky contact barrier between Au/TiO_2 interface. The IV characteristic curves can be explained by the energy band diagram.

Keywords: Schottky Contact, Miro-layer of Au, TiO_2 Nanotubes

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Introduction

TiO_2 is one of the most studied semiconductors in material sciences because of its low cost, long-termstability, non-toxicity, and strong oxidizing power. TiO_2 is an n-type wide band gap semiconductor that can be absorbed UV light irradiation of wavelength about 315-400 nm. However, there are many restrictions to utilize bulk semiconductor as these photodevices because of the high manufactory cost, complicated processing step and photocorrosion. Especially, the bulk semiconductor material corrosions are occurred when they are exposed to light. This phenomenon results in poor chemical stability. Therefore, nanostructure materials with a wide band gap, TiO_2 nanotubes have great interest due easy fabrication, high photocatalytic activity, available abundant, high chemical stability, high surface-to-volume ratios and size dependent properties [1-3]. Therefore, TiO_2 nanotubes can be easily synthesized by anodization method. One of many applications of TiO_2 nanotubes is UV detector in Schottky barrier type. Schottky barrier can be formed if nanolayer metal deposited on semiconductor. Previous studies related to photodetective Titania nanotubes have mainly focused on the investigation of Titania as self-power UV detector [4]. However, the reported that explain the phenomena about occurring Schottky barrier between nanolayer metal deposited on TiO_2 nanotubes have not been published.

This paper is mainly focused on fabrication of Schottky barrier photodiodes on TiO_2 nanotubes surface. The low-cost anodization process was used to synthesize TiO_2 nanotubes. The Au layers were deposited on TiO_2 nanotubes surface by thermal evaporation. Electrical probes were employed to measure the electronic values. Also, the schematic physical diagrams to explain their mechanism were referred to the intra-band dynamic Au/TiO_2 nanotubes.

Materials and Methodology

The 1.5x2.5 cm^2 pieces of Ti foils were used as substrates to form nanotubes in the anodization process. In the first step, these substrates were cleaned in acetone, ethanol and deionized water, respectively, for 15 min in ultrasonic bath. Ti piece was dried by N_2 gas flow. The setup of apparatus was showed in fig. 1. It was composed of two electrode such as Ti foil as anode and graphite sheet as cathode. The mixer solution of 0.3 wt% NH_4F, 12% deionized water in ethylene glycol solvent was used as a chemical bridge solution between two electrodes. After anodization process, the substrate was annealed at 450 ºC for 2 hr with applied temperature constant step at 3.75 °C / min to rearrange the amorphous to crystalline structure.

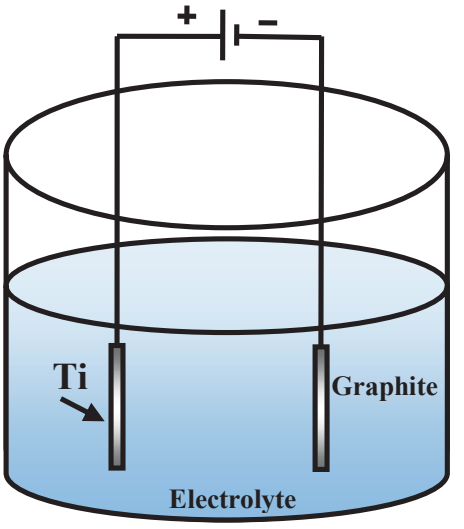

Figure 1 An apparatus of anodization process.

Results and discussion

1. Morphology

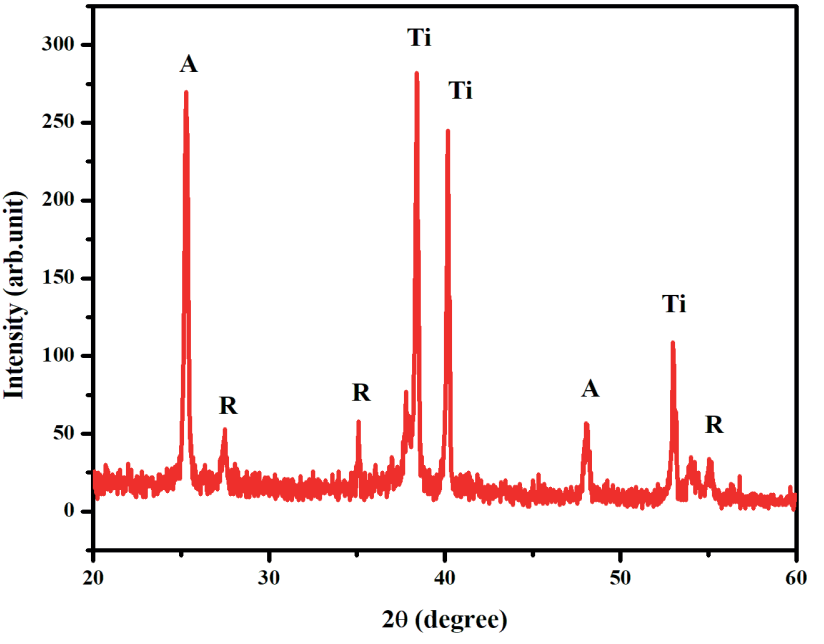

Figure 2 XRD spectrum of TiO_2 nanotubes after annealed at 450 ºC.

In Fig. 2, the XRD spectrum of TiO_2 nanotubes (450 ºC) is shown. The XRD structure consists of the mixing of anatase (2θ = 25.3° and 48°) and rutile (2θ = 27.4°, 35.1° and 53°) peaks. These results correspond with other works [5].

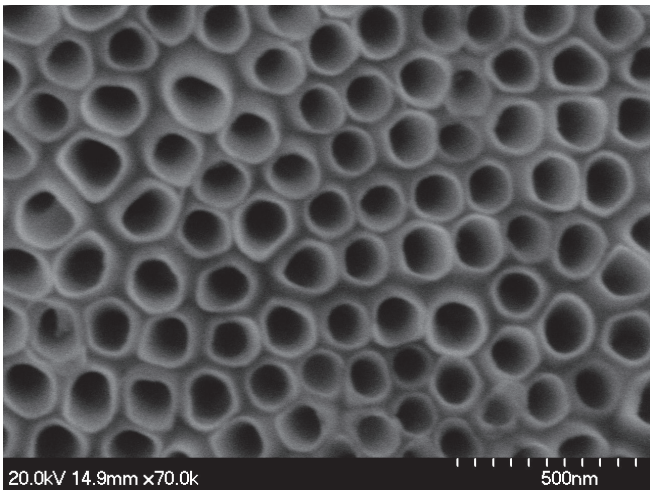

Figure 3 SEM top-view image of TiO_2 nanotubes after annealed at 450 ºC.

The top-views SEM images of TiO_2 nanotubes after annealed with 450 ºC are shown in Fig. 3. The highly ordered nanotubes are obtained with a diameter of 125 nm, wall thickness of 20 nm and tube length of about 2 μm.

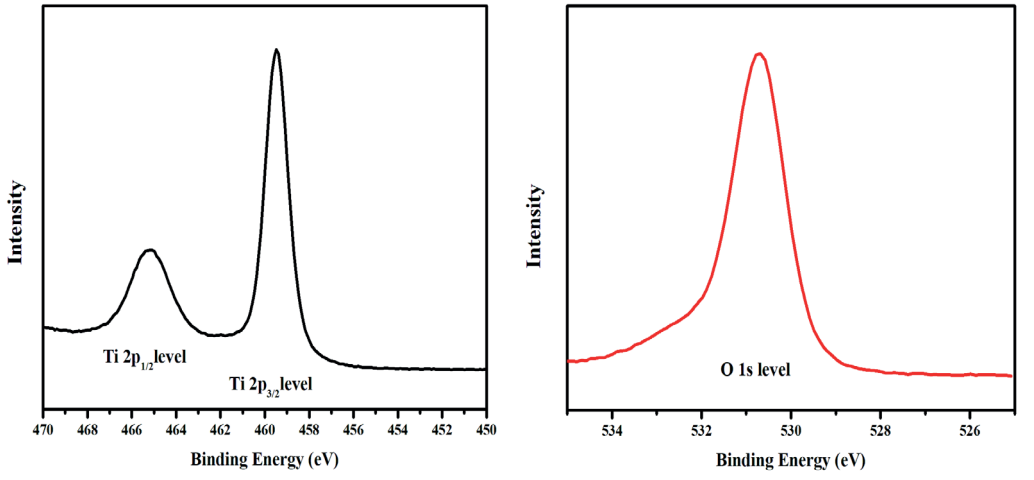

Figure 4 XPS analysis of (a) Ti 2p level and (b) O 1s level.

The presence of TiO_2 nanotubes surface is confirmed by the Ti2p and O1s peaks as shown in Fig. 4(a)., the spin-orbital splitting photoelectrons of $Ti2p_{1/2}$ and $Ti2p_{3/2}$ are located at binding energies of 465.20 and 459.47 eV, respectively. The separated peaks between the $Ti2p_{1/2}$ and $Ti2p_{3/2}$ level are of 5.73 eV. The O1s XPS spectra are shown in Fig. 4(b). The XPS data of TiO_2 nanotubes are in good agreement with the previous reported literature values [6-7].

2. Electronic Properties

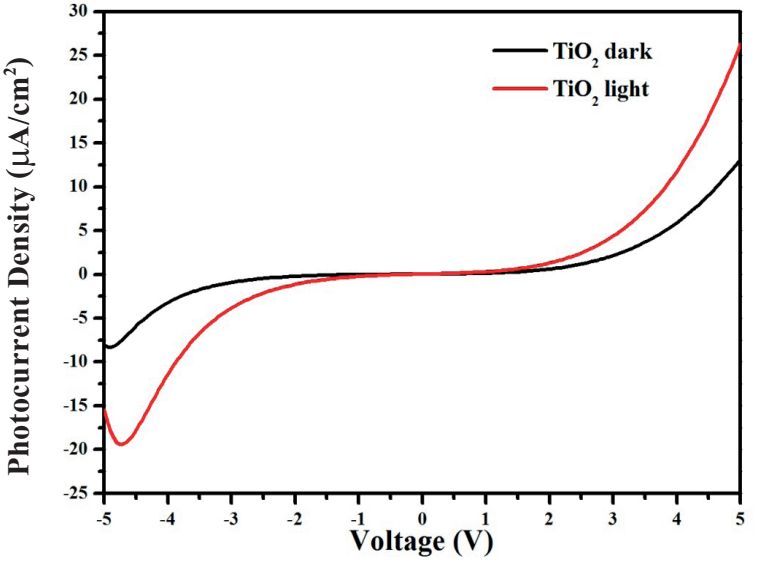

Figure 5 Photocurrent versus voltage curves from applied voltage from -5 V to 5 V of Au/TiO_2 nanotubes.

The two electronic probes method under ambient air condition and room temperature was employed to obtain I-V data. In Fig. 5. at an applied voltage from -5 V to 5 V, the dark current changed from -8μA to 13 μA while the photocurrent changed from-15μA to 25 μA under 365 nm UV light. These show that the fabricated Schottky barrier between Au and TiO_2 nanotubes is occurred.

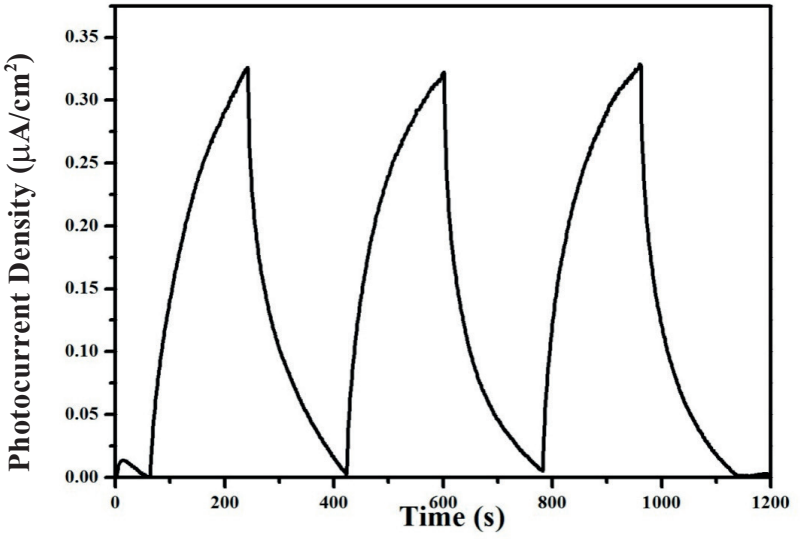

Figure 6 Time-dependent photocurrent of Au/TiO_2 nanotubes.

The time response photocurrent densities measured under biased voltage 1 V of Au/TiO_2 nanotubes is shown in Fig. 6. It indicates that the time response photocurrent densities are exhibited good stability and periodic repeat. In order to focus on the photocurrent, the dark current was set at 0. The irradiation light source (VL-4 LC 4 W) with power density of 350 $\mu W/cm^2$ at wavelength of 365 nm was used. The performance of photosensitive device was determined by two parameters: spectral responsivity (R_s) and external quantum efficiency (EQE) that can be expressed by [8]:

$$R_s = \frac{I_{ph}}{P_0 \cdot S}, \quad (1)$$

where I_{ph} is the difference between illuminated current and dark current $I_{ph} = I_{illuminated} - I_{dark}$, P_0 is the light power density irradiated on devices, and S is the area of devices.

$$EQE = \frac{R_s \cdot hc}{e\lambda}, \quad (2)$$

where h represents the Planck's constant, c stands for the velocity of light, e is the electronic charge and λ is the wavelength of the irradiation light.

The illuminated photocurrent density, spectral responsivity (R_s) and external quantum efficiency (EQE) values are 0.94 mA/W. and 0.0032, respectively.

In Fig. 7., the model of Au/TiO_2 surface are shown. It is one of many types of photodetector called Schottky barrier type UV detector [9]. It is composed of two ohmic contact form from Au deposited on TiO_2 nanotubes then Schottky contact occurred between them. These phenomena can be explained by the inter-band dynamic between Au and TiO_2 nanotubes in Fig. 8(a) and Fig. 8(b).

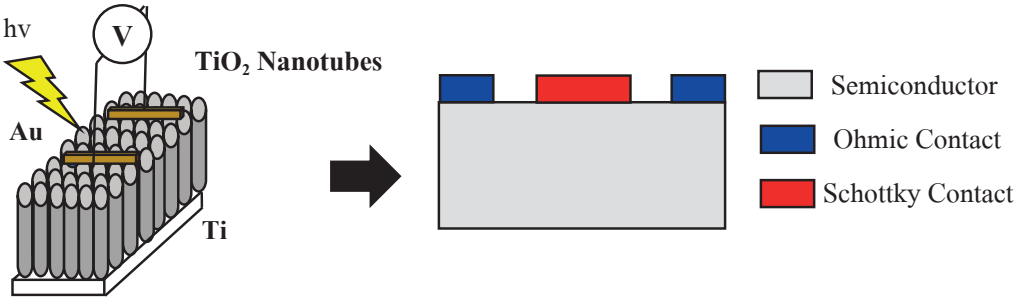

Figure 7 The model of Au/TiO_2 nanotubes showing Schottky barrier.

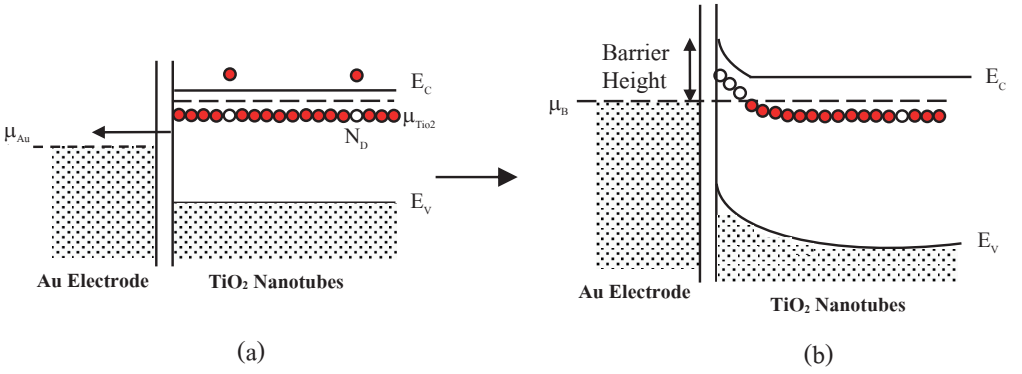

Figure 8 The energy diagram carrier transport mechanisms of Au electrode an TiO_2 nanotubes interface.

TiO_2 nanotubes is n-type semiconductor. The work function of TiO_2 nanotubes is about 4.70 eV [10] while the work function of Au is about 5.40 eV [11]. Therefore, work function value of Au metal is more than work function value of TiO_2 nanotubes resulting in the band edge alignment between Au metal and TiO_2 nanotube surfaces [12]. In Fig. 8 (a), the chemical potential (μTiO_2) of TiO_2 nanotubes is between the donor state (N_D) and the conduction band edge (E_C). They will initially have different chemical potential. On contact charge, electrons will flow from TiO_2 nanotubes to Au metal achieve equilibrium as shown in Fig. 8 (b). These create a region of unbalance positive charge at TiO_2 interface giving rise to band bending. If a positive voltage is applied to Au metal surface in Fig. with respect to TiO_2 nanotube surfaces, the band edge profile in the vicinity of surface gate will be decreasingly bent upward as more as negative charge is attract to Au metal surface gate, filling donor states. This phenomenon contributes to I-V curve from electronic probe measurement.

Conclusions

Schottky barrier can be fabricated by depositing Au on TiO_2 nanotubes surface. These can be confirmed by the two electronic probes. The photocurrent graph in I-V curve increase under 365 nm UV light irradiation. The calculated spectral responsivity and external quantum efficiency from time-dependent photocurrent graph of Au/TiO_2 nanotubes are 0.94 mA/W and 0.0032, respectively.

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References

[1] Mor, G. K., Carvalho, M. A., Varghese, O. K., Pishko, M. V., & Grimes, C. A. (2004). A room-temperature TiO_2-nanotube hydrogen sensor able to self-clean photoactively from environmental contamination. *Journal of Materials Research*, *19*(2), 628–634.

[2] Varghese, O. K., Mor, G. K., Paulose, M., & Grimes, C. A. (2004). A Titania nanotube-array room-temperature sensor for selective detection of low hydrogen concentrations. *MRS Proceedings*, *828*. A3.1/K4.1. DOI: https://doi.org/10.1557/PROC-828-A3.1/K4.1.

[3] Paulose, M., Varghese, O. K., Mor, G. K., Grimes, C. A., & Ong, K. G. (2006). Unprecedented ultra-high hydrogen gas sensitivity in undoped titania nanotubes. *Nanotechnology*, *17*(2), 398–402.

[4] Xie, Y., Huang, H., Yang, W., & Wu, Z. (2011). Low dark current metal-semiconductor-metal ultraviolet photodetectors based on sol-gel-derived TiO_2 films. *Journal of Applied Physics*, *109*(2), 023114.

[5] Su, Y., Han, S., Zhang, X., Chen, X., & Lei, L. (2008). Preparation and visible-light-driven photoelectrocatalytic properties of boron-doped TiO_2 nanotubes. *Materials Chemistry and Physics*, *110*(2-3), 239–246.

[6] Erdem, B., Hunsicker, R. A., Simmons, G. W., Sudol, E. D., Dimonie, V. L., & El-Aasser, M. S. (2001). XPS and FTIR surface characterization of TiO_2 particles used in polymer encapsulation. *Langmuir*, *17*(9), 2664–2669.

[7] Zhu, J., Chen, F., Zhang, J., Chen, H., & Anpo, M. (2006). Fe^{3+}-TiO_2 photocatalysts prepared by combining sol–gel method with hydrothermal treatment and their characterization. *Journal of Photochemistry and Photobiology A: Chemistry*, *180*(1-2), 196–204.

[8] Li, L., Wu, P., Fang, X., Zhai, T., Dai, L., Liao, M., … Golberg, D. (2010). Single-crystalline CdS nanobelts for excellent field-emitters and ultrahigh quantum-efficiency photodetectors. *Advanced Materials*, *22*(29), 3161–3165.

[9] Monroy, E., Omnes, F., & Calle, F. (2003). Wide–bandgap semiconductor ultraviolet photodetectors. *Semiconductor Science and Technology, 18*(4), R33–R51.

[10] Kashiwaya, S., Morasch, J., Streibel, V., Toupance, T., Jaegermann, W., & Klein, A. (2018). The work function of TiO_2. *Surfaces*, *1*(1), 73–89.

[11] Uda, M., Nakamura, A., Yamamoto, T., & Fujimoto, Y. (1998). Work function of polycrystalline Ag, Au and Al. *Journal of Electron Spectroscopy and Related Phenomena, 88-91*, 643–648.

[12] Pierret, R. F. (1996). *Semiconductor Device Fundamentals* (2^{nd} Ed). Massachusetts: Addison-Wesley Publishing Co.